

CHAPTER 3

ELECTROCHEMICAL TECHNOLOGIES AND APPLICATIONS

3.1. ROLE OF ELECTROCHEMICAL TECHNOLOGIES IN CHEMICAL INDUSTRY

3.1.1. Background

The consumption of electricity in the U.S. in the year 2000 was 3,613 billion kWh, of which 890 billion kWh was used by the chemical industry to manufacture a wide variety of chemicals.^{1,2} A breakdown of the energy usage by application in the chemical industry (Table 3.1) indicates that ~130 billion kWh was utilized by the electrochemical industry to generate commodity and specialty chemicals.

3.1.2. Principles of Technologies

Electrochemical processing is an acknowledged means to achieve inter-conversion of electricity and chemicals via reactions at electrode/electrolyte interfaces. Electrons in an electrochemical process are the reagents like the chemicals in chemical reactions. The rate of a chemical reaction, k_c , is dependent on its free energy of activation, ΔG^\ddagger , the reactant concentration, c_r , and temperature, T , as expressed by:

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TABLE 3.1
Breakdown Of Electricity Usage In Electrochemical Operations

Product	Production in 2000 million metric tons	Electric energy consumption, billion kWh
Aluminum	3.78	53.00
Chlorine	14.06	40.00
Sodium chlorate	0.74	4.46
Zinc	0.23	0.75
Copper	1.59	2.00
Manganese	0.76	6.00
Others		24.00

$$k_c = k_c^0 c_r \exp(-\Delta G^\ddagger / RT) \quad (3.1)$$

where k_c^0 is the concentration-independent-rate constant. Thus, increasing the concentration of the reactant and temperature can increase the rate of a chemical reaction. On the other hand, the rate of an electrochemical reaction, k_e , can be described as:

$$k_e = k_e^0 c_r \exp(nF\Delta E^\ddagger / RT) \quad (3.2)$$

where ΔE^\ddagger is the potential difference at the electrode/electrolyte interface and $nF\Delta E^\ddagger$ is equivalent to $-\Delta G^\ddagger$. Hence, the rates of electrochemical reactions can be altered not only by the concentration of the reactants and temperature, but also by changing the potential difference across it by the passage of current. Thus, there is a parallelism between consumption of free energy in a chemical reaction and the electrochemical free energy in an electrochemical process utilizing the passage of electric current. The electrochemical processes have several advantages over the conventional chemical routes, which include:

- control of the rate and selectivity by manipulating the electrode potential;
- high thermodynamic efficiency allowing reactions to proceed at ambient temperatures and pressures;
- pollution-free operation;
- use of less expensive starting materials; and
- reduction in the number of steps involved to make the final product and avoiding the down stream purification steps.

It is because of these benefits that electrochemical technologies have gained commercial status over the last several decades.

Let us now examine the free energy of the reaction $\text{H}_2\text{O} \rightarrow \text{H}_2 + \text{O}_2$. The change in free energy for this reaction ΔG^0 , is 237 kJ/mole. The positive ΔG^0 signifies that the reaction, as written, is not spontaneous. However, by applying a potential above that corresponding to the ΔG^0 of 237 kJ/mole, i.e., 1.23 V, the water

decomposition reaction can be driven in the desired direction. This is the basis for electrochemical processes to produce chemicals. For the reaction of hydrogen and oxygen to form water, ΔG^0 is -237 kJ/mole. Since ΔG^0 for this reaction is negative, the reaction occurs spontaneously. Therefore, one can theoretically extract electrical energy equivalent to that of ΔG^0 per mole of hydrogen. This is the basis for producing electrical energy, be it a fuel cell reaction or other reactions in batteries. It is this capability of inter-conversion of electricity and chemicals that makes the electrochemical processing elegant and attractive. The various technologies that are possible and have been commercialized are presented in Table 3.2.

Electricity is, of course, the primary source of energy supplied to an electrochemical reactor. It drives the reaction and heats the electrolyzer. In practice, the cells sometimes require more electric current than that calculated by the Faraday's law because a part of the electricity is consumed by the side reactions, resulting in coulombic losses. Also, the cell potential is higher than the thermodynamic value due to the overpotentials at the two electrodes and the ohmic overpotentials in the electrolyte and the metallic components (current collectors, electrodes, cables).

The thermodynamic-decomposition potential, E_r^0 , is the minimum potential required for a given electrochemical process to proceed in a given direction and is based on the standard free energy change, ΔG^0 , of the overall reaction as:

$$E_r^0 = -\frac{\Delta G^0}{nF} \quad (3.3)$$

Table 3.2
Leading Electrochemical Technologies

Electrochemistry	
Electrochemical processing	Energy conversion and storage
<ul style="list-style-type: none"> • Electrowinning of metals e.g., Al, Na, Mg, Cu, Ni, Zn • Electrorefining of metals e.g., Al, Au, Cu, Ni, Zn • Production of inorganic chemicals e.g., chlorine/caustic, chlorates, perchlorates • Production of organic chemicals e.g., adiponitile • Corrosion and corrosion prevention • Electroforming and electromachining 	<ul style="list-style-type: none"> • Primary batteries e.g., Leclanche cell • Secondary batteries e.g., lead-acid, Ni-Cd, Ag-Zn • Fuel cells e.g., hydrogen-oxygen • Supercapacitors e.g., carbon and noble-metal oxides

The cell potential corresponding to the heat of the reaction, is:

$$E_t^0 = - \frac{\Delta H^0}{nF} \quad (3.4)$$

and is referred to as the thermoneutral potential, E_t^0 , representing the potential at which neither heat is lost to the surroundings nor required by the system. However, commercial electrolytic cells operate at higher than the thermodynamic decomposition potential to allow the reaction to proceed at the desired rate in the forward direction to generate the desired products. The excess potential, constituting the overpotentials leads to the generation of heat, which should be taken out to ensure isothermal operating conditions of the electrolytic cells.

Let us now exemplify the importance of thermoneutral potential by comparing the E_r^0 and E_t^0 for the electrolysis of HCl solutions. The thermodynamic decomposition potential for the reaction: $\text{HCl} \rightarrow 0.5 \text{ H}_2 + 0.5 \text{ Cl}_2$ is 1.36 V at 25 °C, whereas the thermoneutral potential is 1.74 V. The value of E_t^0 is greater than E_r^0 , since the E_t^0 term contains the heat associated with the entropy change for the reaction. If the cell operates at potentials less than E_t^0 (and above E_r^0), the cell will cool as the cell dissipates the heat corresponding to the entropy change, irreversibly. On the other hand, at voltages higher than E_t^0 , the cell is heated by the excess energy generated by the joule heat caused by the overpotentials and it has to be cooled to operate the cells at a given temperature. The amount of heat generated or absorbed by the system can be calculated as follows. The amount of heat released, Q_{rev} , is given as:

$$Q_{rev} = -T\Delta S = \Delta G^0 - \Delta H^0 = nFE_r^0 - \Delta H^0 \quad (3.5)$$

The cell potential (E) can be written in terms of its constituents as:

$$E = E_r^0 + \Sigma iR + \Sigma \eta_{act} \quad (3.6)$$

where $\Sigma \eta_{act}$ are the activation overpotentials at the anode and cathode.

The irreversible heat generated, Q_{irr} , is given by:

$$Q_{irr} = (E - E_r^0)nF \quad (3.7)$$

Since the heat generated (Q) is equal to $Q_{irr} + Q_{rev}$, Q can be expressed as:

$$Q = nFE - \Delta H \quad (3.8)$$

When Q is positive, heat is released by the system and when Q is negative, heat is absorbed by the system.

The thermoneutral voltage defined by Eq. (3.4) does not reflect the inevitable heat losses from the convection and radiation losses. This was addressed by defining a practical thermoneutral potential, called the *thermobalance voltage*, E_t , by LeRoy et al.^{3,4} for water-electrolysis cells. The thermobalance potential is defined as:

$$E_{tb} = E_{tn} + E_{rad} + E_{conv} \quad (3.9)$$

where E_{rad} and E_{conv} refer to the potential corresponding to the energy losses via radiation and convection, respectively. The E_{rad} and E_{conv} can be estimated using the following equations:

$$E_{rad} = A\varepsilon\sigma(T^4 - T_a^4)10^{-3} / I \quad (3.10)$$

$$E_{conv} = 1.77 A(T - T_a)^{1.25} 10^{-3} / I \quad (3.11)$$

where A is the radiating area (in m^2), ε its emissivity, σ is the Stefan-Boltzmann constant ($5.67 \times 10^{-8} \text{ W/m}^2 \text{ degree}^4$), T_a is the ambient temperature (K), T is the operating cell temperature, and I is the load in kA. Figure 3.1 illustrates the results of the calculations described above for water-electrolysis cells.⁴

The broken line shows the cell voltage as a function of temperature, which crosses with the curve of thermal balance potential at about 90 °C. At temperatures lower than 90 °C, the cell voltage is higher than the thermal balance voltage or the voltage corresponding to the overall requirement of heat, and hence the cell dissipates excess heat, which must be removed. On the other hand, at temperatures higher than 90 °C, the heat generation is insufficient to compensate for the total heat required for the reaction so that the cell has to be heated. Thus, the cell can be operated at about 90 °C without any heating and/or cooling. The discussion, presented above, emphasizes the need to seek the optimal conditions to realize effective utilization of the energy.

Another important consideration towards achieving energy savings in an electrolytic process is an understanding of the energy needed for the electrolytic cell, which is directly proportional to the cell potential and inversely proportional to the cell efficiency. Components, constituting the cell potential and cell efficiency, should be clearly understood to pursue options to realize energy savings. These aspects will be discussed in the following Sections in the context of the technologies presented in this Chapter. The intent of this Chapter is to (i) provide a brief

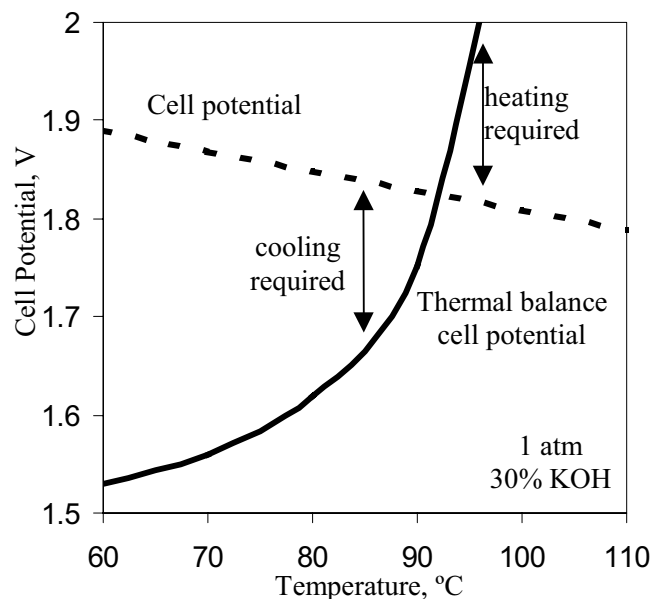


Figure 3.1. Isothermal and thermal-balance cell potentials (E) of a water electrolyzer as a function of temperature at 1 atm total pressure. Reproduced from Reference 4, Copyright (1983), by permission of The Electrochemical Society, Inc.

description of some important electrochemical technologies and (ii) demonstrate benefits to or from fuel cell technologies. Two of the well-developed hydrogen energy technologies, i.e., electrolytic-hydrogen production (which has also been commercialized) and fuel cells (which are in an era of the beginning of commercialization) are not included in this Chapter. The former is presented in Chapter 8 and the latter in Chapters 4, 9, and 10.

3.2. ALUMINUM PRODUCTION

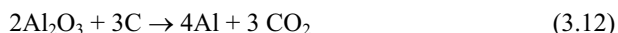
3.2.1. Background and Applications

The world production of aluminum was 23 million metric tons in the year 2001 and about 11 % of it was produced in the U.S.A. Aluminum is a lightweight and strong material that is used in a wide variety of engineering and construction applications. It has also been used to replace copper as the conductor of electricity.

Domestic consumption of aluminum for transportation is 35 %, while 25 % is for packaging, 8 % for consumer durables, 7 % for electrical, and 11 % for others.⁶⁻⁸

3.2.2. Principles of Technology

Aluminum is produced by the molten salt electrolysis of Al_2O_3 dissolved in Na_3AlF_6 by the Bayer-Hall-Hèrault process. This process is over 100 years old and is the only technology used in the world to produce this metal. The overall reaction to produce aluminum is:



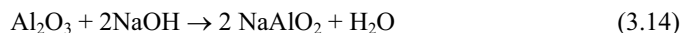
the cathodic reaction being the reduction of Al^{3+} to Al and the anodic reaction being the oxidation of C to CO_2 . The changes in the enthalpy and the free energy of this reaction at 1250 K (977 °C) are -547.6 kJ/mol and -338.6 kJ/mol, respectively, and the entropy change is -168 J/mol K. The free energy change of the reaction corresponds to a reversible cell voltage of 1.18 V. The stoichiometric consumption of carbon is 0.33 tons/ton of Al, which may be compared to the actual consumption of 0.4–0.5 tons/ton of Al in commercial cells.

Aluminum can also be produced by the electrolysis of Al_2O_3 as:



However, the reversible voltage for this reaction is 2.21 V vs. 1.18 V for the reaction (3.12). Thus, while the use of carbon anodes results in the consumption of carbon and generation of CO_2 , reaction (3.12) has the advantage of allowing the operation of the aluminum electrolysis cells at a lower voltage.

Alumina required for the Hall-Hèrault process is produced from bauxite ores by the Bayer process. Bauxite contains 55–60 % Al_2O_3 , 5–10 % Fe_2O_3 , 3–7 % SiO_2 and a small amount of TiO_2 along with water, depending on the source. Since SiO_2 forms an insoluble $\text{Na}_2\text{O} \cdot x\text{Al}_2\text{O}_3 \cdot y\text{SiO}_2$, ores with low silica are preferred for the Bayer process. Briefly, the Bayer process consists of calcining the ore with caustic at 350–500 °C to remove organics and water, followed by grinding it to 20 mesh size or smaller in ball mills. It is then extracted with caustic at 150–170 °C to form sodium aluminate, as expressed by the equation:



When the NaOH concentration in the reaction mixture is ~40–50 % by weight and the Al_2O_3 : NaOH concentration ratio is 0.55–0.65, the solution is filtered to remove “red mud” which is mostly an oxyhydroxide of Fe. The filtrate is then transferred to a hydrolysis tank, where it is seeded at 50 to 70 °C to facilitate the formation of

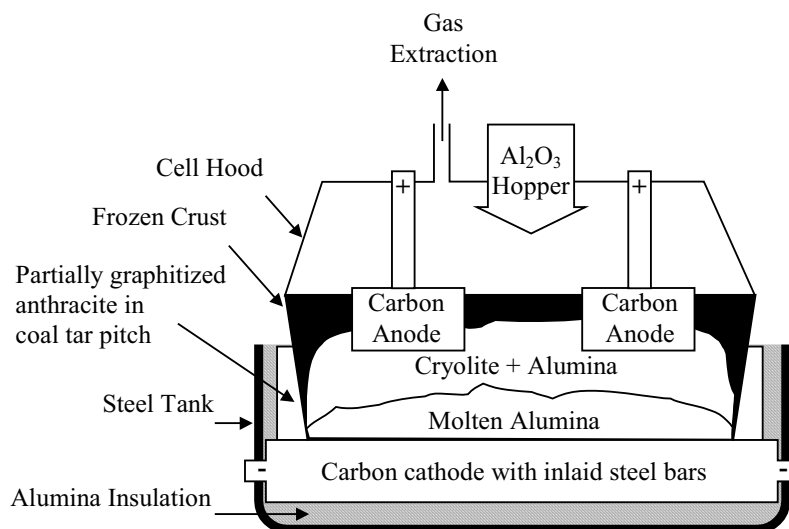


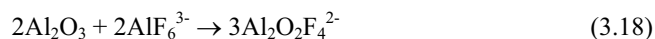
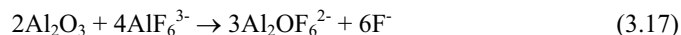
Figure 3.2. Electrochemical cell for the Hall-Heroult process for aluminum production. Reprinted from Reference 5.

aluminum hydroxide precipitates. The aluminum hydroxide is then filtered and calcined in a rotary kiln at 1200–1300 °C to form α -Al₂O₃. Electrolysis is conducted at 975 °C in cells consisting of a steel shell, lined with alumina that acts as a refractory, thermal insulator, and then with carbon. The cells are typically 9–16 m x 3–4 m x 1.0–1.3 m in size. The base of the tank is lined with pre-baked carbon blocks with inlaid steel bars to lower electrical resistance. The sides are lined with partially graphitized anthracite in coal tar pitch. During electrolysis, a layer of solid cryolite and alumina forms at the sides of the cell and a solid crust on the surface, which acts as a barrier to corrosion and heat losses from the cell. The cell has provision for periodic addition of alumina through the crust and for removal of aluminum by suction. Figure 3.2 depicts a typical Hall-Heroult cell.

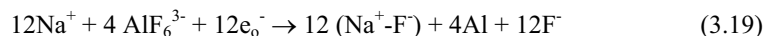
Although not completely understood, the reactions participating in the cathodic deposition of aluminum⁶ and anodic oxidation of carbon are generally believed to follow the scheme noted below. Cryolite ionizes in the following:



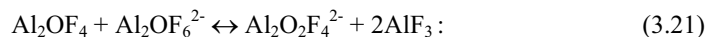
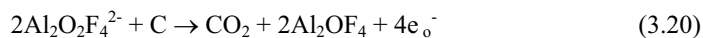
Alumina forms complex oxyfluoride ions depending on the concentration of alumina. At low concentrations of alumina, $\text{Al}_2\text{OF}_6^{2-}$ is formed according to Eq. (3.17), and at high concentrations, $\text{Al}_2\text{O}_2\text{F}_4^{2-}$ is formed according to Eq. (3.18):



The cathodic reaction is generally assumed to be:



The anodic reaction involves the discharge of oxyfluoride ions to form CO_2 and AlF_3 :



Combining Eqs. (3.17) and (3.20) results in the overall reaction (3.12). Aluminum produced by the Hall-Hèrault process is 99.9 % pure, but still contains small amounts of impurities such as Si (0.05 %) and Fe (0.05 %). This purity is generally sufficient for most end uses. However, some markets require high quality aluminum. Hence, it is further purified in a specially designed three-phase electrolyzer, to produce 99.995 % aluminum.

3.2.3. Economics

The capital cost involved in manufacturing aluminum varies with the size of the plant and its location. Capital costs for a new plant for producing aluminum are \$5000/ton of installed annual capacity, whereas the capital costs for producing alumina are \$1000/ton of annual capacity. The average operating costs vary widely depending on the source and location, as shown in Table 3.3. On an average, the power costs vary from > 30 mils/kWh for high cost smelters in Asia to as low as 9.7 mils/kWh in Canada, and 18.2 mils/kWh in the western world.

TABLE 3.3
Operating Costs (\$/Ton Of Aluminum) in 1998

	Western World	Russia	China
Power	283	230	586
Alumina	351	491	469
Other materials	238	302	267
Labor	118	40	25
Other costs	164	174	190
Total	1154	1236	1536

TABLE 3.4
Consumption of Raw Materials for Producing 1 Ton of Aluminum

Raw materials	Weight, kg	Electricity, kWh	
Alumina	1948	DC power for electrolysis	15,338
Cryolite	29	Losses in bus bar and rectifier	413
Recovered cryolite	21	For melt	68
Aluminum fluoride	32		
Anode paste	585		
Coke	420		
Pitch	188	Labor (man h)	
Cathode carbon	15	Direct	2.03
		Indirect	1.07

Table 3.4 shows the consumption of raw material and energy requirements for the production of aluminum. This data shows that the major component of the energy usage in aluminum production is the electricity for operating the cells, which is $\sim 13\text{--}15$ kWh/kg of aluminum.⁹⁻¹¹

3.2.4. Energy Conservation Measures

The theoretical energy requirement for producing Al is 60×10^6 kJ/ton of Al (assuming 30 % energy efficiency), whereas the process needs are five times higher, electrolysis alone consuming three times the theoretical energy needs. As a result, there has been a major focus towards lowering the energy consumption and significant progress was made to reduce the energy consumption from ~ 28 kWh/kg of Al in the 1920s to $13\text{--}15$ kWh/kg of Al. The breakdown of the energy consumption in terms of the components of cell voltage shows (see Table 3.5) that the ohmic drop between the anode and cathode is one of the major contributors to the cell voltage.

The need for the large anode-cathode gap of 5 cm in the cells arises as a consequence of the instability of the aluminum pool from the intense magnetic fields. The large anode-cathode gap minimizes the shorting of the electrodes and

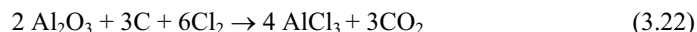
TABLE 3.5
Components of Cell Voltage of Aluminum Electrolyzer (with Pre-Baked Anodes)

Decomposition voltage, E_{th}^0	1.60 V
IR ohmic drop in electrolyte, IR_e	1.45 V
Anode overpotential, η_a	0.30 V
Cathode overpotential, η_c	0.40 V
IR ohmic drop in hardware, IR_{hw}	0.10 V
Anode effect	0.15 V
Total cell voltage	4.00 V

the chemical reaction of the products of the reaction, which results in lower current efficiency. It is interesting to note that in the aluminum cell the joule heat is effectively used to maintain the temperature at $\sim 1000^\circ\text{C}$. The use of carbon anodes in the Hall-Héroult cells causes several problems, which include: CO_2 emissions, generation of perfluorinated carbon compounds at the anode, disposal of cyanide contaminated spent pot-lining, and unpleasant working conditions. These factors coupled with the high-energy needs forced the aluminum manufacturers to examine measures to avoid these problems. Two types of carbon anodes used are the prebaked and self-baking ones (also called Soderberg anodes). The Soderberg anodes are fed at the top with the ground carbon and a pitch binder, which bakes in situ as the anode is lowered into the molten electrolyte to form a hard, dense anode material. The Soderberg anodes are used as they eliminated the anode-manufacturing step. However, the in situ baking process created fumes that are difficult to control. Therefore, the industry reverted to the use of prebaked anodes. Except for the design of anodes, the industry has changed little since the last century.

Three approaches that were pursued to achieve energy conservation and environmental benignity are (i) electrolysis of AlCl_3 , (ii) development of non-consumable TiB_2 anodes, and (iii) refractory hard metal (RHM) composite cathodes.

- (a) *Electrolysis of AlCl_3* . Alcoa examined the electrolysis of AlCl_3 to produce Al and Cl_2 . The chlorine generated in this process can be used to prepare AlCl_3 as shown in the equation:



The advantages of this route include lower overall consumption of carbon and 10% better energy efficiency than the Hall-Héroult process.

- (b) *TiB_2 anodes*. The use of titanium diboride anodes will eliminate the need to use the carbon anodes and thereby avoid the environmental problems noted earlier. However, the thermodynamic decomposition voltage will be higher since the anode reaction is the discharge of oxygen. This approach was investigated extensively and only recently has it been brought to a commercial stage. DeNora North America developed the “Veronica Anode”, which is a TiB_2 -based anode with long life and low solubility in cryolite, and a Moltech Tinor 2000 cathode that is a Ni-Fe alloy with special additives such as Cu, Al, Ti, Y, Mn, and Si to improve corrosion resistance. Pilot tests⁸ have shown a wear rate of $\sim 3 \text{ mm/yr}$ at current densities greater than 1.1 A/cm^2 . Preliminary estimates show a savings of 20 % of the production cost and 2.5 % increase in cell life.
- (c) *RHM cathodes*. It is necessary for the cathode to be wetted with a thin film of aluminum, which would drain to a sump and provide a stable cathode surface. Presently, the aluminum deposited on the cathode stays on the cathode as a pool. This pool sloshes due to the

electrohydrodynamic effect and as a result, the anode is kept away to prevent shorting and to prevent the recombination reaction.

3.2.5. Benefits to or from Fuel Cell Technologies

Though there is no apparent benefit to or from fuel cell technologies, aluminum will be a useful material for fabrication of some fuel cell components. As an example, thin aluminum sheets coated with graphitic carbon or gold are being considered as candidate materials for the construction of bipolar plates.

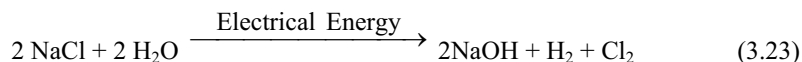
3.3. CHLOR-ALKALI TECHNOLOGY

3.3.1. Background and Applications

Chlor-alkali technology is one of the largest electrochemical industries in the world, the main products being chlorine, sodium hydroxide (also called as caustic soda), and hydrogen generated simultaneously by the electrolysis of sodium chloride. It is an energy intensive process. The chlor-alkali industry is the second largest consumer of electricity (next to aluminum) among the electrochemical industries, accounting for about 40 billion kWh of electrical energy consumed for the production of 14.06 million short tons of chlorine in the year 2000. Chlorine and caustic soda are indispensable intermediates for the chemical industry. Chlorine is a strong oxidizer and has the largest volume use in the production of vinyl chloride monomer, which, in turn, is polymerized to polyvinyl chloride (PVC). Chlorine is also widely used as a bleaching agent, especially in the pulp and paper industry, and as a disinfectant, as for example in swimming pools. Chlorinated organic compounds, such as chlorinated ethanes and fluorocarbons are used as intermediates in the manufacture of polymers, like polyesters and urethanes. Caustic soda, on the other hand, has wide industrial applications in mineral processing, the pulp and paper industry, and the textile and glass manufacturing operations.

3.3.2. Principles of Technology

Electrolysis of aqueous solutions of sodium chloride (NaCl), commonly referred to as brine, simultaneously generates chlorine, caustic soda (or potash), and hydrogen according to the overall chemical reaction:



Reaction (3.23) has a positive free energy change of 422.2 kJ/mol of chlorine at 25 °C. Therefore, dc-electrical energy has to be provided to force the reaction to

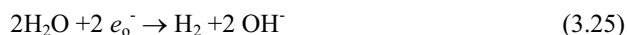
proceed in the forward direction. The amount of electrical energy required depends on the amount of the product needed and the electrolytic cell parameters, current density, and cell potential—the latter being dictated by the nature of the anode and cathode material, the separator, the inter-electrode gap, and the cell design.^{12–15}

Production of chlorine, caustic, and hydrogen from brine is accomplished in three types of electrolytic cells: the mercury cell, the diaphragm cell, and the membrane cell. The distinguishing characteristic of these cells is the manner in which the electrolytic products are prevented from mixing with each other. In Figure 3.3 a comparison is made of the three types of cells and Figures 3.4 to 3.6 show schematics of the process flow diagrams for these technologies.

The primary electrochemical reactions, which occur during the electrolysis of brine, are the discharge of the chloride ion at the anode to form chlorine:



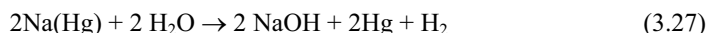
and the generation of hydrogen and hydroxide ions, OH^- , at the cathode:



Chlorine is generated at the anode in all the three types of electrolytic cells. The cathodic reaction in diaphragm and membrane cells is the electrolysis of water to generate hydrogen as shown by Eq. (3.25), whereas the cathodic process in mercury cells is the discharge of the sodium ion, Na^+ , to form sodium amalgam, containing 0.2 to 0.3 % sodium:



This amalgam subsequently reacts with water in denuders, or decomposers, to generate hydrogen and caustic:



Separation of the anode and cathode products in diaphragm cells is realized using an asbestos polymer-modified asbestos composite, or a non-asbestos material deposited on a mesh cathode. In membrane cells, the separator is a cation-exchange membrane. Mercury cells require no diaphragm or membrane, because the mercury itself acts as a separator.

The catholyte from diaphragm cells typically contains 9–12 % caustic soda and 14–16 % NaCl. This cell liquor is concentrated to 50 % NaOH in a series of evaporation steps involving three or four stages. Membrane cells produce 30–35 % NaOH, which is evaporated in two or three stages to produce 50 % caustic soda.

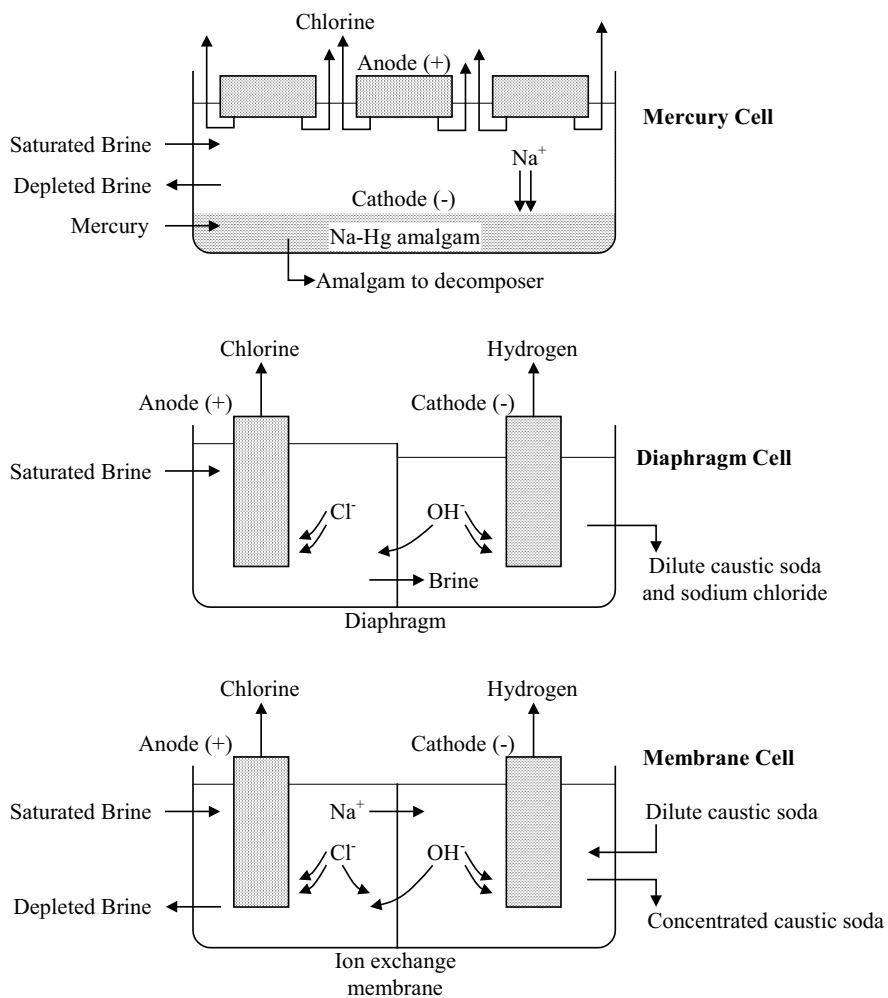


Figure 3.3. Schematics of the three types of chlor-alkali cells.

The 50 % caustic soda, containing very little salt, is made directly in the mercury cell process by reacting the sodium amalgam with water in the decomposers.

The anodes, used in all these three cell technologies, are ruthenium oxide and titanium oxide coated titanium, which operate at a low chlorine overpotential with excellent dimensional stability and long life. The cathode material in diaphragm cells is made of carbon steel and exhibits an overpotential of 300–400 mV for the

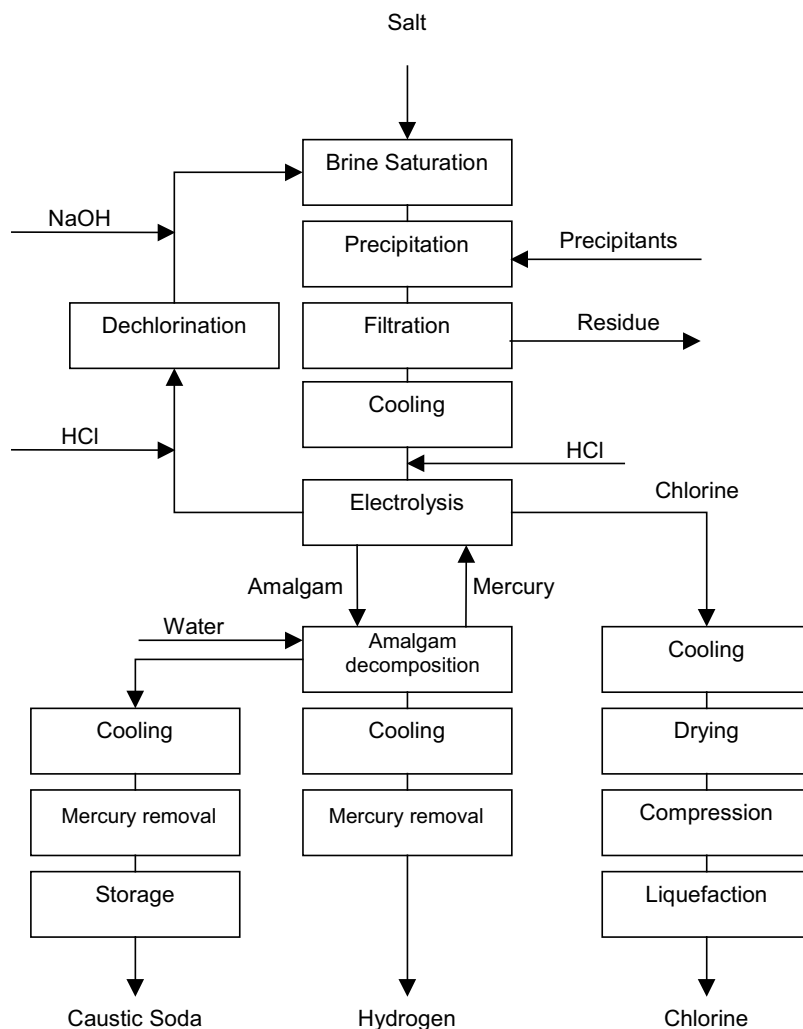


Figure 3.4. Flow diagram of the Mercury cell process for chlor-alkali production. Reproduced from Reference 12, Copyright (1985), with permission from John Wiley and Sons, Inc.

hydrogen evolution reaction. Energy savings, by reducing the overpotential as much as 200–280 mV, are achievable, in principle, by using nickel cathodes with a catalytic coating. The coatings that are commercially employed in membrane cells

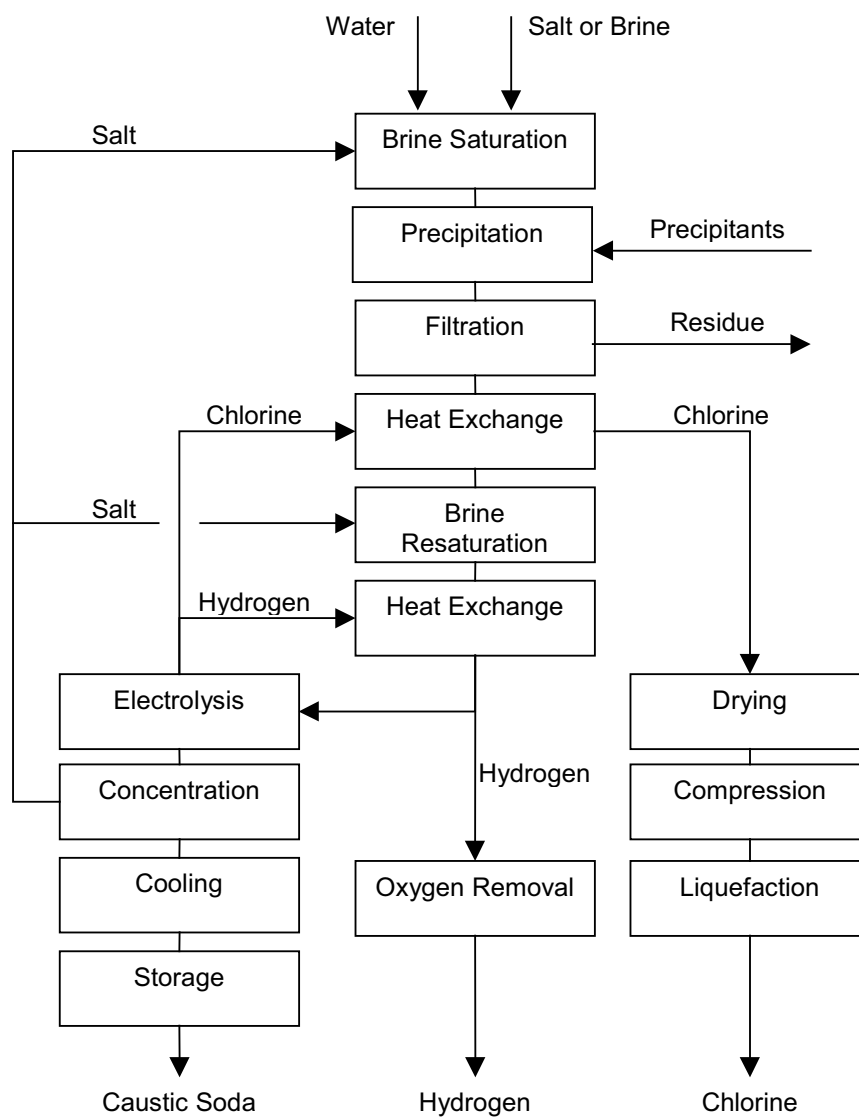


Figure 3.5. Flow diagram of the Diaphragm cell process for chlor-alkali process. Reproduced from Reference 12, Copyright (1985), with permission from John Wiley & Sons, Inc.

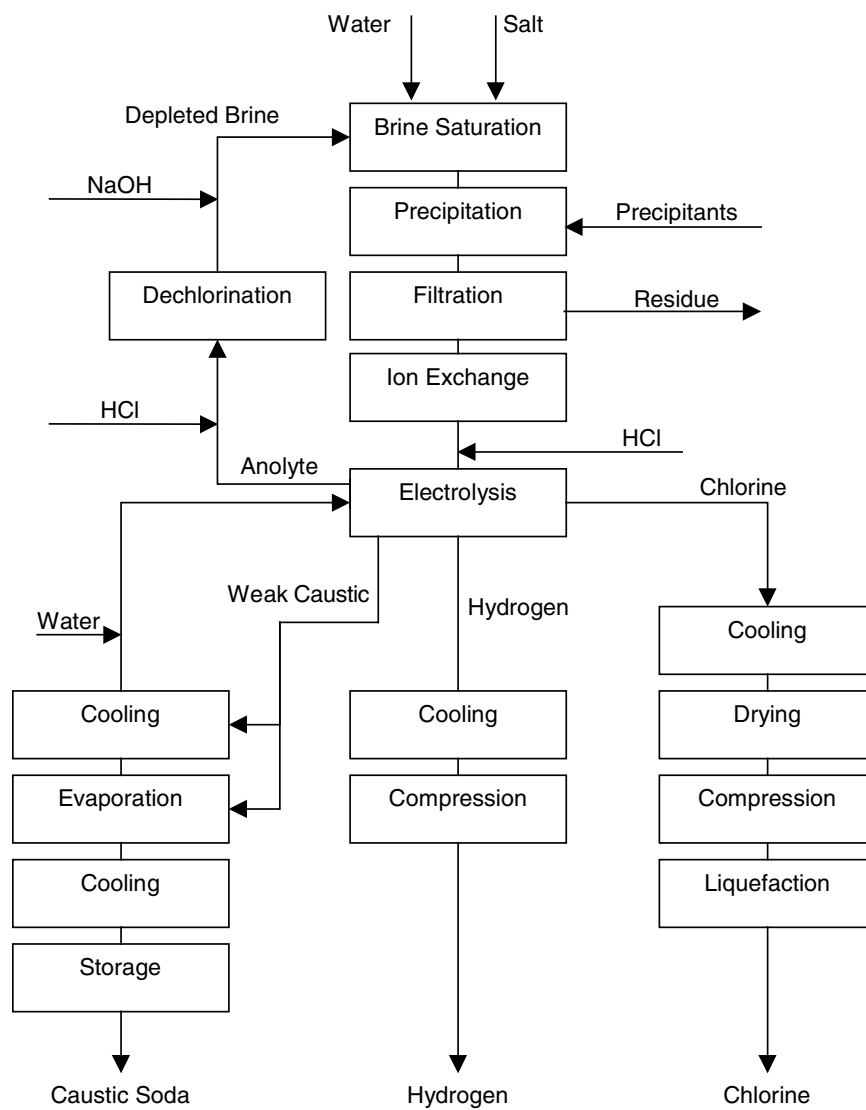


Figure 3.6. Flow diagram of the Membrane process for chlor-alkali production. Reproduced from Reference 12, Copyright (1985), with permission from John Wiley & Sons, Inc.

are nickel-sulfur, nickel-aluminium, nickel-nickel oxide mixtures, and nickel coatings containing the platinum group metals. Although electrocatalytic cathode technology is utilized in membrane cells, commercialization is still awaited in diaphragm cells.

The membrane is a critical component of the membrane-cell technology as it determines the current efficiency, cell voltage, and hence the energy consumption for the production of chlorine and caustic soda. The membranes currently used are composite membranes with perfluorosulfonic acid layers facing the anolyte side and perfluorocarboxylic acid layers facing the catholyte side, with an intermediate reinforcing fabric between them. These composite membranes provide high current efficiency and low cell voltage at current densities above 5 kA/m². These composite membranes are prepared by lamination of the perfluorocarboxylate and perfluorosulfonate films, by the chemical conversion of the perfluorosulfonic acid to realize a carboxylate layer thickness of 5–10 μm, or by co-extension of the two different polymer films, which will provide high efficiency with a low voltage penalty.

The minimum energy required to produce chlorine, hydrogen, and caustic from salt is the same (i.e., 1686.32 kWh/ton of chlorine) for all three cell technologies. However, the actual energy consumed is much higher than the minimum. The energy consumed in the mercury-cell process is the greatest because the combined voltages required by reactions (3.26) and (3.27) are higher than those encountered in the diaphragm or membrane-cell processes.

Electrolysis of brine (Eq. 3.23) is endothermic. The overall heat of the reaction is 446.68 kJ/mol (106.76 kcal/mol of chlorine) and hence, the thermoneutral voltage, i.e., the voltage at which heat is neither required by the system nor lost by the system to the surroundings, would therefore be 2.31 V. In practice, however, chlor-alkali cells operate in the range of 3.0 to 3.5 V, at an average coulombic efficiency for chlorine production (*CE*) of 95 %, resulting in heat generation to the extent of 3960 kJ/kg of Cl₂ for a cell potential (*E*) of 3.5 V as derived from the following equation:

$$Q = \left[\left[\frac{100}{CE} \right] [46.05 \text{ V}] \right] - \Delta H \quad (3.28)$$

Heat produced in these cells operating at voltages of above 2.31 V is generally removed by water evaporation and radiation losses. Figure 3.3 illustrates the basic principles of the three cell processes and Table 3.6 summarizes the differences in the cell technologies and their performances.

The values of energy consumption presented in Table 3.6 are not optimal for the indicated technology, since the actual value depends on the current density, cell voltage, and current efficiency, which are affected by the process variables. Similarly, the energy for evaporation varies with the type of the evaporator system used. In the case of membrane cells, the energy requirements would be 15–25 % lower than those for diaphragm cells—the major savings resulting from caustic

TABLE 3.6
Comparison of Components and of Performance Characteristics of Membrane, Diaphragm, and Mercury Cells in Chlor-Alkali Plants

Component	Mercury Cell	Diaphragm Cell	Membrane Cell
Anode	RuO ₂ + TiO ₂ coating on Ti substrate	RuO ₂ + TiO ₂ + SnO ₂ on Ti substrate	RuO ₂ + IrO ₂ + TiO ₂ coating on Ti substrate
Cathode	Mercury on steel	Steel (or steel coated with activated nickel)	Nickel coated with high area nickel based or noble metal based coatings
Separator	None	Asbestos, polymer-modified asbestos, or nonasbestos diaphragm	Ion-exchange membrane
Cathode product	Sodium amalgam	10-12% NaOH + 15-17% NaCl + 0.04-0.05% NaClO ₃ , and H ₂	30-33% NaOH + <0.01% NaOH and H ₂
Decomposer product	50% NaOH and H ₂	None	None
Evaporator product	None	50% NaOH with ~1.1% salt and 0.1-0.2% NaClO ₃	50% NaOH with ~0.01% salt
Steam consumption	None	1500-2300 kg/t NaOH	450-550 kg/t NaOH
Cell voltage, V	4-5	3.0-4	2.8-3.3
Current density, kA/m ²	7-10	0.5-3	2.0-10.
Energy consumption (kW h/ton of Cl ₂)			
Electricity for electrolysis	3200-3600	2800-3000	1950-2220**
Steam for caustic evaporation*	0	600-800	200-350***
Total	3200-3600	3400-3800	2150-2570
* 1 ton of steam = 400 kW h ** Load: 3-6 kA/m ² *** MP steam(10 bar a, 200 °C) double effect evaporator			

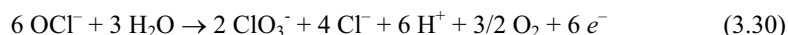
evaporation. Thus, the energy needed to concentrate 33 % NaOH to 50 % caustic can vary from 720 kWh/ton of caustic to 314 kWh/ton, depending on whether a single effect or a triple effect is used for caustic concentration.

There are several inefficiencies arising from parasitic reactions occurring at the electrodes and in the bulk, which are described below. The two parasitic reactions offsetting anode efficiency are:

- co-generation of oxygen, from the anodic discharge of water:

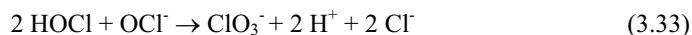


- electrochemical oxidation of hypochlorite ion, OCl^- , to chlorate, ClO_3^- :

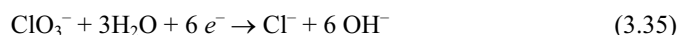
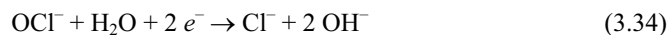


The oxygen generated from these reactions is dependent on the nature of the anode material and the pH of the medium. The current efficiency for oxygen evolution is generally 1–3% when using commercial metal anodes.

At the cathode, water molecules are discharged to form gaseous hydrogen and hydroxide ions, OH^- . Some of the caustic generated in the cathode compartment back migrates to the anode compartment and reacts with dissolved chlorine ($\text{Cl}_{2,\text{aq}}$) to form chlorate as follows:



There are two reactions that influence the cathodic efficiency, namely the reduction of OCl^- and ClO_3^- :



Although these reactions are thermodynamically possible, they are not kinetically significant under normal operating conditions. Hence, the cathodic efficiency is usually high (> 95 %) in diaphragm and membrane cells. In mercury cells, the cathodic inefficiency arises from the discharge of H_2 at the cathode as a result of the impurities in the brine. Reactions contributing to anodic inefficiency in mercury cells are the same as in diaphragm or membrane cells.

Of the three electrolytic technologies used to produce chlorine and caustic, diaphragm-cell technology is the source for generating the largest volume of chlorine, followed by the membrane-cell process, and then the mercury process.

However, the membrane process is the preferred technology for the future because of its ecological and economical benefits over the other two technologies. Over the past ten years, neither new diaphragm nor mercury plants have been built. Depending on operating parameters (i.e., current density, cell voltage, and current efficiency), the electrical energy consumption in membrane chlor-alkali electrolysis is between 1950 and 2300 kWh/t of chlorine. The amount of energy required to concentrate caustic soda from 32 wt% to 50 wt% varies between 700 and 800 kWh/t (basis: medium pressure steam) of chlorine for a double-effect evaporator. The electrical energy consumption in diaphragm chlor-alkali electrolysis is about 10 to 20 % higher than that for the membrane technology. In addition, diaphragm cells generate caustic soda at a low concentration of ~ 11 wt%, and hence, the energy requirements to achieve the commercial concentration of 50 wt% of caustic soda are much higher compared to the membrane process. The current membrane technology suppliers are: Asahi-Kasei, Chlorine Engineers, Uhde, ELTECH, and INEOS Chlor.

3.3.3. Economics

The choice of technology, the associated capital, and operating costs for a chlor-alkali plant are strongly dependent on the local energy and transportation costs, as well as environmental constraints. The primary difference in operating costs between membrane, diaphragm, and mercury plants results from variations in electricity and steam consumption for the three processes. The cost of constructing a grass root plant significantly depends on the actual plant configuration, procurement conditions, and of course, the production capacity. A breakdown for the total investment for a grass root membrane electrolysis plant of about 160,000 Mt/y of chlorine production capacity is presented in Table 3.7.

Conversions from mercury to membrane technology require new facilities to protect the membranes from traces of mercury and place restrictions on the use of existing equipment. Diaphragm plants are often more easily adapted to the needs of membrane technology.

3.3.4. Benefits to or from Fuel-Cell Technologies

Adopting fuel-cell based technologies can significantly lower the energy consumption involved in manufacturing chlorine. One approach, that is particularly applicable for diaphragm-cell operations, involves concentrating the weak diaphragm cell catholyte from ~ 10 – 12 % to 50 % NaOH. This scheme involves feeding the diaphragm caustic to the anode compartment of a membrane cell and using the hydrogen ionization reaction as the anodic process when the protons released by the anodic process will neutralize the hydroxyl ions in the anolyte. The cathodic reaction in this scheme is the discharge of water to form hydrogen and the

TABLE 3.7
Typical Cost Breakdown For A Chlor-Alkali Plant

Item	Estimated investment in 1000 US\$
Cells	27,200
Brine purification	14,000
Chlorine processing	16,000
Waste gas treatment	2,300
Caustic evaporation	6,900
Utilities	4,500
Rectifiers	10,000
Engineering	10,000
Total	90,900

hydroxyl ions in the catholyte. Occidental Chemical Corporation has examined this concept. However, it has not proceeded beyond the laboratory stage.

Another fuel cell based idea involves substituting an oxygen-reduction reaction for the hydrogen-evolution reaction at the cathode in chlor-alkali electrolysis. This will reduce the total cell potential by about one volt (theoretically 1.23 V), thereby realizing a substantial electrical energy savings of > 900 kWh/short ton of chlorine. The anode reaction is the same as in a conventional chlor-alkali cell, where the chloride ions are discharged to form a chlorine gas product and the sodium ions migrate to the cathode compartment through the ion-exchange membrane. At the cathode, oxygen is reduced to the OH^- ions, which combine with the Na^+ ions to form sodium hydroxide. The oxygen consumed in this reaction enters the air cathode compartment either as water-saturated pure oxygen gas or as air and gets reduced at the porous air cathode (a fuel cell cathode). The additional advantages of using the oxygen-reduction reaction include avoidance of costly downstream-treatment of hydrogen and absence of the gas void fraction in the catholyte, resulting in a reduced ohmic drop in the cell. However, this scheme requires a high-performance air scrubbing system to remove all carbon dioxide from the air in order to protect the air cathode from the accumulation of sodium carbonate and a premature failure of the cells. As the anode side of the process does not differ from the conventional chlor-alkali cell, these components can be used without any modification.

However, the cathode side has several special needs, the central one being the adjustment of the local differential pressure between the caustic and the oxygen compartment on the other side of the electrode. Due to the porous nature of the gas-diffusion electrode (GDE), a pressure balance across the electrode has to be established in order to avoid the flow of the fluid from one side to the other. The local differential pressure is a function of height because of the different densities of the fluids, and it can be made small using two different approaches. The first one involves splitting the cathode compartment into several horizontal compartments,

called gas pockets in which the height of each sub-compartment limits the hydrostatic pressure of the caustic to a tolerable value. The lean caustic flows through the pockets successively, by overflowing from one pocket to the next one below. This *gas-pocket principle* is patented and now being tested by the Bayer AG group. A second approach to the problem is the *falling-film principle*. The development of this type was initiated by the Hoechst group in the 1980's and is presently continued by Uhde. The idea here is to decrease the hydrostatic pressure of the caustic successively by establishing a falling film of caustic between the electrode and the membrane. This is realized by means of a layer of hydrophilic material, which is fixed between the anode and the cathode. This design ensures a constant gap between the GDE and the membrane itself. Because of the electroosmotic water transport from the anolyte to the catholyte, the caustic flow increases from the top to the bottom of the cell. A high flow in the hydrophilic layer will lead to a flooding of the GDE, and hence a breakthrough of caustic into the oxygen-compartment, caused by an increased differential pressure. This flooding can be avoided by a proper design of the hydrophilic layer. The falling-film technology shows some inherent advantages. Unlike the gas-pocket principle, the falling-film technology does not need an extensive gasket system throughout the surface of the GDE, allowing a simplified design. Furthermore, the GDE can be run close to the atmospheric pressure, so that it will always operate in the optimum operating pressure range. Both processes show comparable operating data. However, they are still at an experimental level. Nevertheless, the initial results with the GDE system are promising towards achieving an energy savings of ~30 %, compared to the conventional membrane process.^{16,17}

An alternate approach to reduce energy consumption is to use the hydrogen generated in the chlor-alkali process in a fuel cell to extract the same energy benefits as retrofitting or developing a cell with oxygen cathodes.

3.4. ELECTRO-ORGANIC SYNTHESIS

3.4.1. Background and Applications

Electro-organic synthesis dates back to at least 1834 when Faraday described the anodic oxidation of acetate ions to carbon dioxide.¹⁸ It was fifteen years later that Kolbe discovered the generation of n-butane by the electrolysis of aqueous valeric-acid solutions. Since then a large number of industrially important organic compounds were synthesized and several of them were commercialized. Table 3.8 describes some on-going commercial processes. There are many other fine chemicals that are produced electrochemically, but they remain in the proprietary domain.

TABLE 3.8
Some Current Electroorganic Technologies

Product	Starting Material	Company
Acetoin	Butanone	BASF
Acetylenedicarboxylic Acid	1,4-Butynediol	BASF
Adipoin Dimethyl Acetal	Cyclohexanone	BASF
Adiponitrile	Acrylonitrile	Monsanto (Solutia), BASF, Asahi Chemical
4-Aminomethylpyridine	4-Cyanopyridine	Reilly Tar
Anthraquinone	Anthracene	L. B. Holliday, ECRC
Bleached Montan Wax	Raw Montan Wax	Hoechst
Calcium Gluconate	Glucose	Sandoz, India
Calcium lactobionate	Lactose	Sandoz, India
S-Carbomethoxymethylcysteine	Cysteine and Chloroacetic	Spain
L-Cysteine	L-Cystine	Several
Diacetone-2-ketogluconic Acid	Diacetone-L-sorbose	Hoffman-LaRoche
Dialdehyde Starch	Starch	India, Others
1,4-Dihydronaphthalene	Naphthalene	Hoechst
2,5-Dimethoxy-2,5-dihydrofuran	Furan	BASF
2,5-Dimethoxy-2,5-dihydrofuryl-1-ethanol	Furfuryl-1-ethanol	Otsuka
Dimethylsebacate	Monomethyladipate	Asahi Chemical
Gluconic Acid	Glucose	Sandoz, India
Hexafluoropropyleneoxide	Hexafluoropropylene	Hoechst
Mucic Acid	Galacturonic Acid	EDF
Perfluorinated hydrocarbons	Alkyl substrates	3M, Bayer, Hoechst
Phthalide and t-Butylbenzaldehyde Acetal	Dimethyl Phthalate and t-Butyltoluene	BASF
p-Methoxybenzaldehyde	p-Methoxytoluene	BASF
Polysilanes	Chlorosilanes	Osaka Gas
p-t-Butylbenzaldehyde	p-t-Butyltoluene	BASF, Givaudan
Salicylic Aldehyde	o-Hydroxybenzoic Acid	India
Succinic Acid	Maleic Acid	CECRI, India
3,4,5-Trimethoxybenzaldehyde	3,4,5-Trimethoxytoluene	Otsuka Chemical
3,4,5-Trimethoxytoluoyl Alcohol	3,4,5-Trimethoxytoluene	Otsuka Chemical

3.4.2. Principles of Technology

The initial step during the course of an electrochemical reaction involving an organic molecule is generally the formation of a reactive radical or radical ion as:

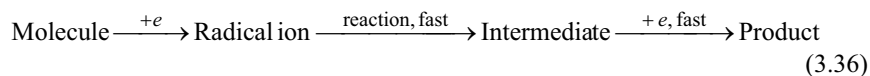


TABLE 3.9
Classification of Electroorganic Reactions

1. Direct: Charge transfer is the primary act with the organic substrate of interest.	
a. Cation radical formation	$R \rightarrow R^+ + e^-$
b. Anion radical formation	$RX \rightarrow RX^{\cdot-} - e^-$ where X may be halogen, H or other functional group.
c. Carbonium ion formation	$RH \rightarrow R^+ + H^+ + 2e^-$ e.g., $CH_3-COO^- \rightarrow CH_3^+ CO_2 + 2e^-$
d. Carbanion formation	$RX + 2e^- \rightarrow R^- + X^-$
e. Reduction of carbonium ions or oxidation of anions	1. $R^- + e^- \rightarrow R^{\cdot}$ e.g., $\phi-CH=N^+(CH_2)_4 \rightarrow \phi-C^+H-N(CH_2)_4 \rightarrow \text{product}$ (dimerizes on reaction) 2. $R^- \rightarrow R^{\cdot} + e^-$ e.g., $CH_3COO^- \rightarrow CH_3CO_2 + e^-$ \rightarrow dimerizes
2. Indirect: Charge transfer occurs with some other species, which then reacts with the substrate of interest.	
a. With electrogenerated redox species	e.g., Cr^{6+} , Ce^{4+} , Ag^{2+} , Br_2 , etc.
b. With adsorbed intermediates generated during the course of a reaction	e.g., Cl_{ads} , CO_2^- , $HO_2^- (ads)$, H^+ or OH^-

The manner by which the electron transfer can occur can be direct or indirect, as shown in Tables 3.9 and 3.10. The electrochemically generated radicals (radical anions or cations) react in a multitude of pathways, either chemically or electrochemically to form a wide variety of products. These reaction pathways could become more involved when adsorbed intermediates interact with these species. Figures 3.7 and 3.8 depict some of these reaction sequences that can occur with radical cations and anions from unsaturated hydrocarbons.

Thus, a wide variety of organic reactions can be performed electrochemically, the basic processes being anodic oxidation or cathodic reduction often without the use of any other chemical reagents. Generally, desirable concentrations of highly reactive cation or anion radicals can be easily generated electrochemically. Other reactive species that can be conveniently made include superoxide ions, hydroxyl radicals, peroxide, CO_2 , anion radicals, hydrogen atoms, and halogens, including fluorine. Another advantage with electrochemical routes for organic synthesis is the role played by the electrode materials, which could alter the course of reactions. Some examples of the influence of electrode materials are shown in Figures 3.9 to 3.12 to illustrate the specificity that can be achieved electrochemically.

TABLE 3.10.
Indirect Electrolysis for Electroorganic Syntheses.

Redox Couple	Electrochemical Conversion
$\text{Ti}^{4+}/\text{Ti}^{3+}$	Nitroaromatics \rightarrow anilines, Quinine \rightarrow hydroquinone
$\text{Fe}^{3+}/\text{Fe}^{2+}$	Acrylonitrile polymerization
$\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$	Benzene oxidation
$\text{MnO}_4^-/\text{MnO}_4^{2-}$	Oxidation of aromatics
$\text{Ni}^{3+}/\text{NiF}_6^{2-}$	Electrofluorination
$\text{Ti}^{3+}/\text{Ti}^{+}$	1-Butene to methyl ethyl ketone
$\text{Co}^{3+}/\text{Co}^{2+}$	Oxidation of aromatics
$\text{Sn}^{4+}/\text{Sn}^{2+}$	Reduction of nitrocompounds
$\text{Ce}^{2+}/\text{Ce}^{3+}$	Anthracene to anthraquinone
$\text{Cu}^{2+}/\text{Cu}^{+}$	Hydroxylation of aromatics
$\text{VO}_3^-/\text{VO}^{2+}$	Oxidation of aromatics
$\text{HIO}_4/\text{HIO}_3$	Dialdehyde starch process
NaHg/Hg	Hydrodimerization
NaOCl/NaCl or NaOBr/NaBr	Propylene oxide from propylene or Oxidation of sugars
$\text{OsO}_4/[\text{OsO}_2(\text{OH})_4]^{2-}$	Olefins to glycols
Br_2/Br^-	Alkoxylation of furans
I_2/I^-	Halofunctionalization; Prevost reaction

Electrofluorination of organic compounds occurs at only a few anode materials (Figure 3.9). These include nickel in HF solution, porous carbon in molten HF/KF, and Pt in organic solvents containing fluoride ion. The nickel anode leads to nonspecific fluorination apparently involving nickel hexafluoride (NiF_6^{2-}) ionic species as the fluorinating agent. This high-valent species is formed as an insoluble, continuously renewable anode surface coating that attacks the organic. The porous carbon anode employed in the Phillips electrofluorination process also leads to nonspecific fluorinations by the electrogenerated fluorine atoms. In contrast, platinum behaves differently because the organic is directly oxidized to a cationic species, which then undergoes nucleophilic attack by the fluoride ions.

Depending on the choice of the cathode material, acetone can be converted to isopropyl alcohol, pinacol, propane, or diisopropyl mercury (Figure 3.10). The mechanism involved in the formation of isopropyl alcohol is direct, but the formation of di-isopropyl mercury is a result of the interaction of electrogenerated radical species with the mercury cathode by metal-atom abstraction.

The diversity of products formed during the electroreduction of nitrobenzene depends largely on the nature of the cathode material, the solvent and the supporting electrolyte, and other factors such as temperature and reactant concentration (Figure 3.11). The selectivity depends on the nature of and stability of the intermediates formed and the rates at which the consecutive reactions proceed either in the bulk or at the interface. These factors dictate the appropriate choice of the hydrodynamic regimes in the cell that allow the reactions to proceed at significant rates in the

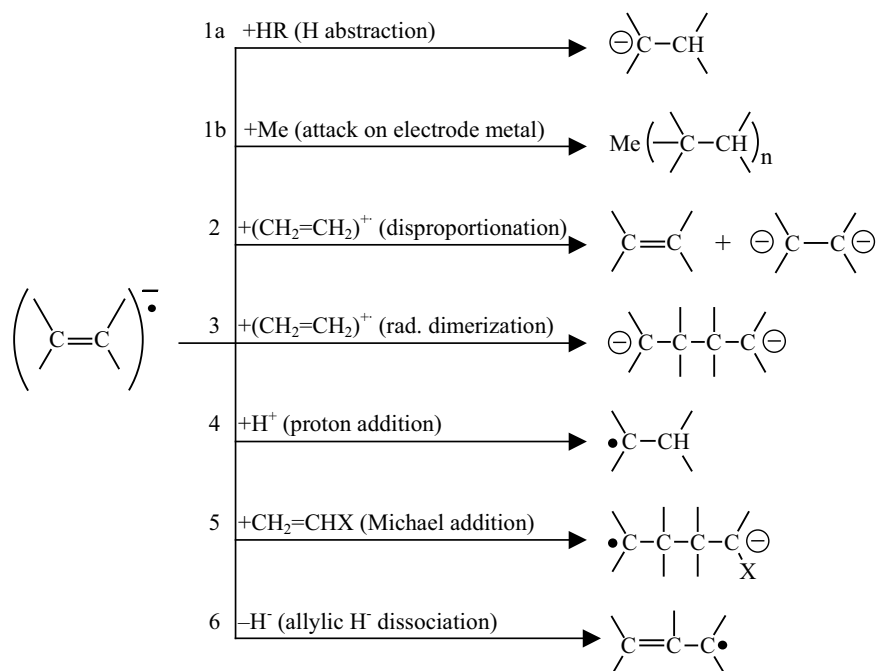


Figure 3.7. Reaction routes [6] for radical anions from unsaturated hydrocarbons (e.g., vinyl compounds): (1-3) radical reactions; (4-6) anionic reactions. Reproduced from Reference 19.

desired direction. It must be emphasized that the penalties associated with poor selectivity and low yields are enormous, as the overall process economics would be adversely affected by the high-energy requirements and the costs involved in the separation and purification of the products.

Hydrodimerization of acrylonitrile provides a further example of the role of the substrate in organic synthesis (Figure 3.12). Thus, acrylonitrile is reduced to propionitrile at Pt and Ni cathodes by adsorbed H atoms, whereas on Pb electrodes allylamine is formed. Sn electrodes yield the organometallic and Hg, Pb, and C cathodes lead to the formation of adiponitrile and propionitrile. The large-scale electro-organic industry, at present, is the Monsanto process for producing adiponitrile by the electrohydrodimerization of acrylonitrile. The estimated total production of adiponitrile worldwide is ~340,000 tons/year, and this product is an intermediate for manufacturing Nylon-66. The chemical route for making adiponitrile is the catalytic reaction of adipic acid with ammonia, which is then converted to hexamethylenediamine and finally to Nylon-66 as shown below:

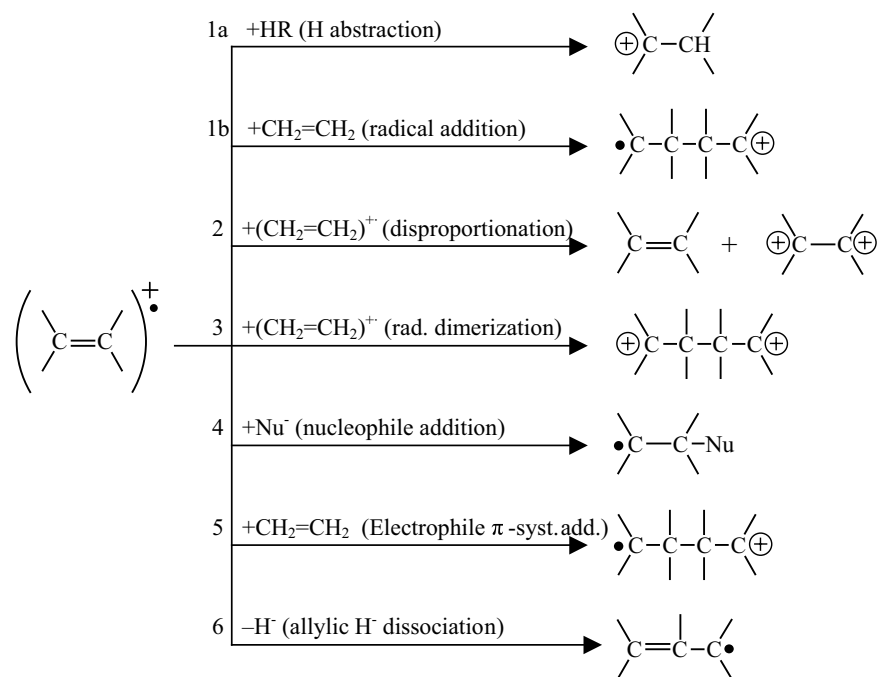
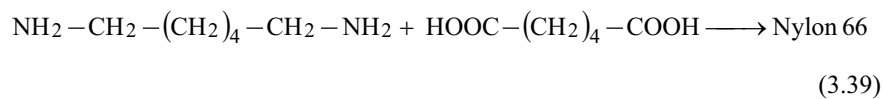
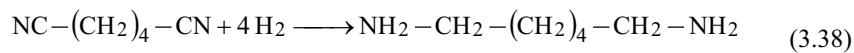
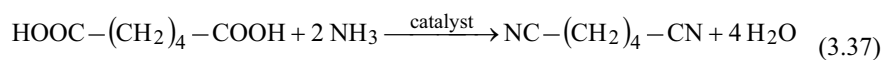


Figure 3.8. Reaction routes [6] for radical cations from unsaturated hydrocarbons: (1-3) radical reactions; (4-6) cationic reactions. Reproduce from Reference 19.



The driving force for the electrochemical route to produce adiponitrile from acetonitrile is the high cost of adipic acid. This process was discovered by M. Baizer in 1959, and was commercialized by D. Danly at the Monsanto Corporation. Basically, the reaction involved is the electrohydrodimerization of acrylonitrile as follows:

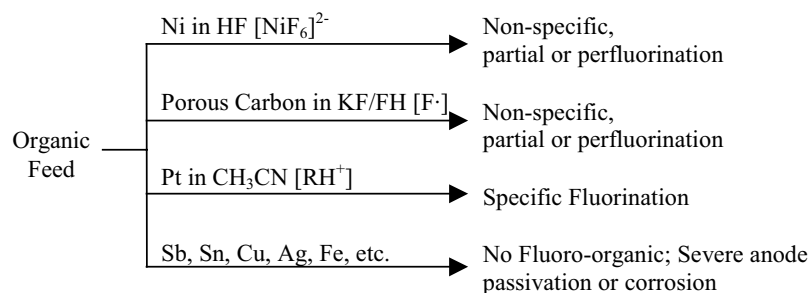
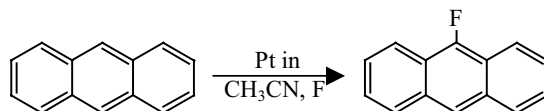
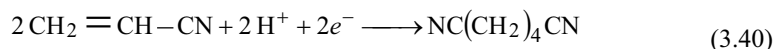
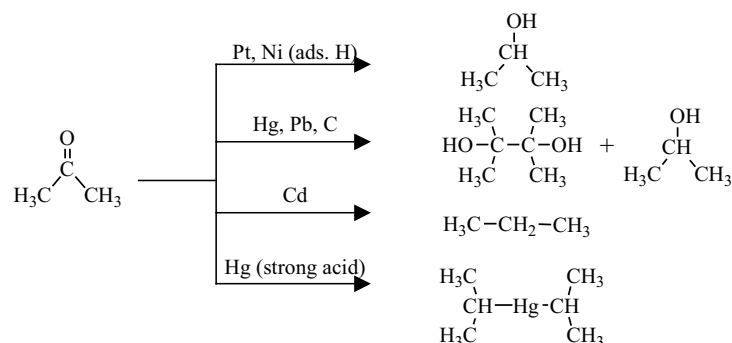
Examples

Figure 3.9. Influence of electrode material during electrofluorination. Reprinted with permission from Reference 20, Copyright (1979), American Chemical Society.



The early Monsanto process used a two-compartment cell with Pb cathodes and $\text{PbO}_2 + \text{AgO}$ anodes, separated by a cation exchange membrane. The catholyte was 40 % tetraethyl ammonium sulfate containing 28 % water, 16 % acetonitrile and, 16 % acrylonitrile, the anolyte being 5 % sulfuric acid. This process, although successful, suffered from several problems such as membrane fouling, low conversion rates, byproduct formation, high-energy consumption of 6700 kWh/ton of adiponitrile, and expensive product isolation processes. All these problems were addressed, and a new Monsanto process was developed in the late 1970's (see Figure 3.13).

This second generation process is based on an undivided cell and employs Cd cathodes and steel anodes in a bipolar cell configuration. The electrolyte is a two-phase recirculating aqueous emulsion of acrylonitrile, adiponitrile, a bisquaternary salt (hexamethylene (bisethyltributyl) ammonium phosphate), a phosphate buffer, and anode anti-corrosion additives, borax, and EDTA. Electrolysis is conducted at 55 °C at 2 kA/m². A fraction of the organic phase is continuously removed from the



Some of the electrogenerated species involved:

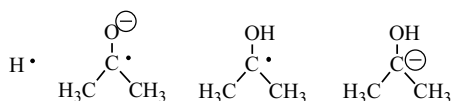


Figure 3.10. Influence of electrode material on the electrochemical reduction of acetone. Reprinted with permission from Reference 20, Copyright (1979), American Chemical Society.

emulsion reservoir for separation of the product. The aqueous phase is also reacted continuously to prevent accumulation of byproducts and metallic salts from electrode corrosion. Table 3.11 depicts a comparison of these processes.

TABLE 3.11.
Comparison of the Monsanto 1965 Divided Cell Process With the Recent Monsanto Undivided Cell Process.

	Divided cell	Undivided cell
Adiponitrile selectivity (%)	92	88
Inter-electrode gap (cm)	0.7	0.18
Electrolyte resistivity (Ω cm)	38*	12
Electrolyte flow velocity (ms^{-1})	2	1-1.5
Current density (A cm^{-2})	0.45	0.20
Voltage distribution (V)		
Estimated reversible cell voltage	2.50	2.50
Overpotentials	1.22	0.87
Electrolyte iR	6.24	0.47
Membrane iR	1.69	0.87
Total	11.65	3.84
Energy consumption (kW h t^{-1})	6700	2500

*catholyte

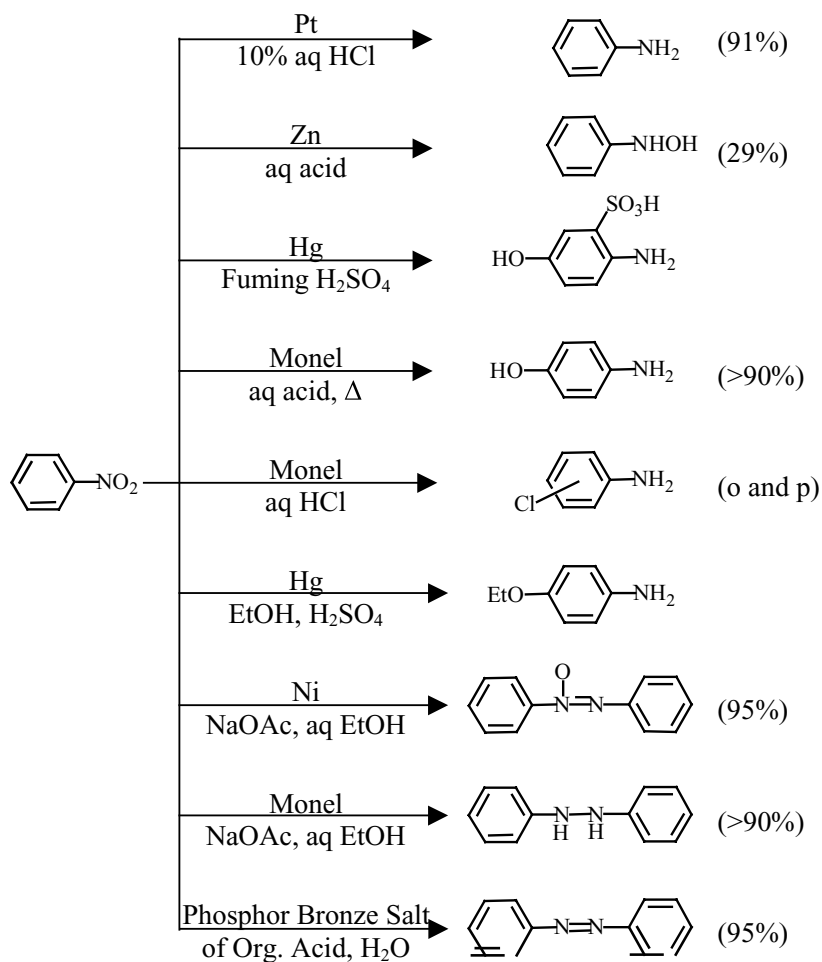


Figure 3.11. Influence of electrode material during electrochemical reduction of nitrobenzene. Reprinted with permission from Reference 20, Copyright (1979) American Chemical Society.

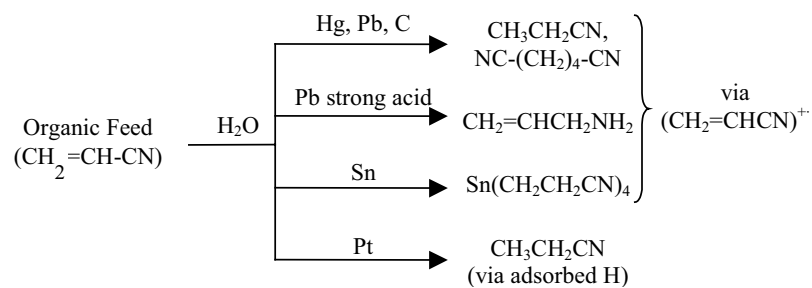


Figure 3.12. Influence of electrode material during hydrodimerization of acrylonitrile. Reprinted with permission from Reference 20, Copyright (1979), American Chemical Society.

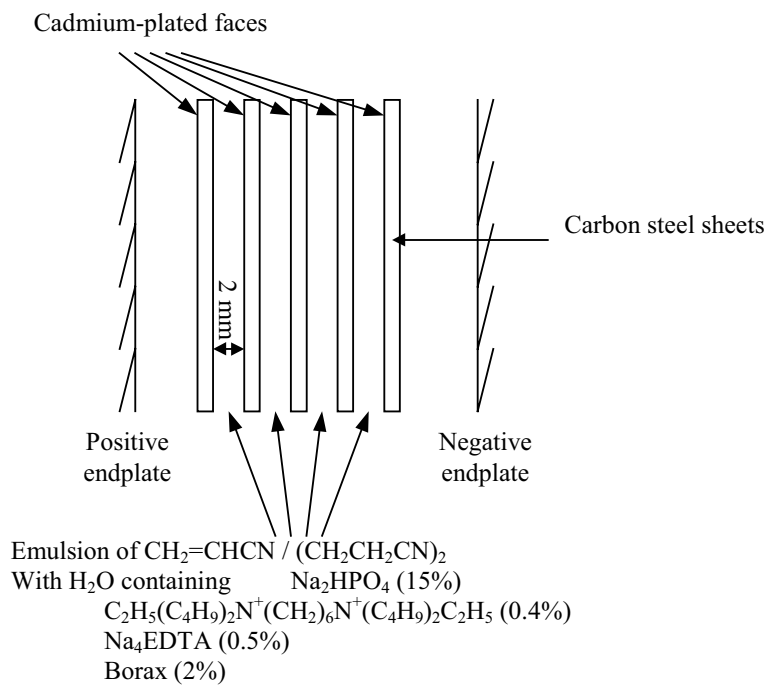


Figure 3.13. The new Monsanto process for the hydrodimerization of acrylonitrile.²⁰

3.4.3. Economics

Generally, in electroorganic processes, 6–15 % of the operating costs are towards electricity and 20–70 % for the starting materials. The investment costs towards the electrochemical cell can vary between 5 to 50 % depending on the specific process. Adiponitrile (ADN) made by the Monsanto process is an intermediate for making hexamethylene diamine (HMDA), which is then converted to Nylon-66. The capital costs for producing 100,000 kg/year of HMDA were estimated to be \$101MM in 1987,^{21,22} of which about \$61MM are for processing AN to HMDA. Since the yield of HMDA from ADN is 96.6 %, the capital costs for producing about 100,000 kg/year will be about \$50MM, the cost of the undivided electrolytic cells being \$7.5 MM and the power system being \$0.9 MM. The total direct production costs for this capacity of HMDA are \$0.26/kg of which the raw materials cost is \$.49/kg and electricity cost is \$0.03/kg at an electricity price of \$0.05/kWh.

3.4.4. Benefits to or from Fuel Cell Technology

Depending on the type of organic reaction that is being conducted at the working electrode, the electrode reaction at the counter electrode is either the hydrogen evolution or the oxygen evolution reaction. These reactions can be supplanted by the oxygen reduction reaction or the hydrogen ionization reaction, as long as the organic species in the solution are not reacting at these interfaces, to achieve significant energy savings. The idea of using fuel-cell reactions in electroorganic syntheses was proposed in 1984.²³⁻²⁵ The hydrogen ionization reaction was studied as the anodic reaction during the hydrodimerization of acetonitrile and a voltage savings of 400 mV at 100 mA/cm² was claimed with a gas diffusion electrode containing a platinum catalyst.²⁴ Another process that was examined using the hydrogen depolarized anode was the hydrodimerization of formaldehyde to ethylene glycol. Efficiencies as high as 90 % for ethylene glycol formation were obtained²³⁻²⁵ with the hydrogen depolarized anode in an undivided cell. However, the low molecular weight compounds such as formaldehyde and methanol were oxidized at the anode, resulting in the generation of > 80 % CO₂ on the back side of the gas diffusion electrode. A third process examined with the anodic reaction as the hydrogen ionization reaction was the reduction of 3-hydroxybenzoic acid to the corresponding benzylic alcohol in a divided cell in aqueous sulfuric acid solutions. These investigations showed a 40% reduction in the cell potential, relative to a divided cell of comparable construction. Thus, while the investigations with the fuel cell based electroorganic reactions are limited, the results show significant potential towards achieving energy savings in these operations.

3.5. ELECTROWINNING AND REFINING OF METALS

3.5.1. Background and Applications

Almost all metals exist in their native state as oxides or sulfides. The sulfide ores are calcined, leached with sulfuric acid, and the resulting sulfate solution is electrolyzed to produce high quality metals. The large tonnage metals, produced electrolytically, are copper, nickel, and zinc; cobalt, chromium, manganese, cadmium, gallium, thallium, indium, silver, and gold are produced by electrolysis on a smaller scale. The annual production amounts of copper, nickel, and zinc were 13.2, 0.37 and 8.7MM tons, respectively, in 2001.⁵

Zinc is used for metallic coatings to protect iron and steel for corrosion protection by galvanizing, plating, and painting with zinc-bearing paints. Its use, as a structural material, is for pressure die-casting alloys for automotive and builders' hardware, foundry alloys, and slush alloys. Zinc dust and powder find extensive use in atomizing process, paint coatings, as a reducing agent to produce hydrosulfite compounds for the textile and paper industries and to enhance the physical properties of plastics and lubricants. Zinc powder is also used in primary batteries, frictional materials, spray metallizing, mechanical plating, and chemical formulations. 55% of the zinc produced is galvanizing, 17% for Zn-based alloys, 15% for making brass and bronze, and 15% for others.^{7,26}

The largest single market for refined copper is for electrical uses because of its high electrical conductivity. 40 % of the total consumption of copper is for building construction (i.e., electrical products, plumbing goods, and roofing sheet). An average modern U.S. home contains about 200 kg of copper. It is also used for transportation and industrial machinery equipment. Other uses include coinage, agricultural fungicides, wood preservatives, food additives, utensils, and cutlery. About 39% of the copper is consumed in the building construction, 28 % for electric and electronic products, and 11% each for transportation equipment, industrial machinery and equipment, and consumer and general goods.^{7,27}

Nickel is used to produce a wide range of corrosion- and heat-resistant materials by alloying with copper, chromium, iron, molybdenum, and others. Pure nickel powder is employed in the production of porous plates for batteries and powder metallurgy parts. 39% of the nickel is produced for stainless steel and alloy steel production, 38 % for non-ferrous and super alloys, 15% in electroplating, and 15% for others.^{7,28}

3.5.2. Principles of Technology

The processes of electrowinning and electrorefining generally employ a similar process scheme. In electrorefining, plates of crude metal are anodically dissolved in a suitable electrolyte, while pure metal is deposited on the cathode. Electrorefining is practiced to produce copper, lead, nickel, silver and other minor metals. The

soluble anode, used in nickel refining, is nickel matte containing 20% sulfur. This process is similar to refining with a metallic anode, but it is not a true refining process and is called electrowinning with a soluble anode. A process that is related to electrorefining is electrowinning with insoluble anodes. In this process, the metal present in the ore is leached from the calcined ore and then the pure metal is “electrowon” with insoluble anodes. Thus in both processes, the cathodic reaction is the reduction of the cationic species, of interest, in the solution to the metallic state, whereas the anodic reaction is the anodic dissolution of the metal from the impure electrode and in some cases the oxygen evolution reaction (in electrowinning operations).

In an ideal electrorefining process, the metal deposition and dissolution reactions take place under nearly reversible conditions. Impurities, which are more electropositive to the electrorefined metal will not dissolve at this potential and will end up in the anode slime. Metals, which are electronegative to the refined metal, will dissolve anodically and accumulate in the electrolyte but will not deposit on the cathode. This simple description applies well to the metals with low dissolution and deposition potentials and with impurities for which the standard reversible electrode potentials are sufficiently different from that of the refined metal.

Selectivity^{5, 29} for the anodic process is often helped by the refractory nature of the impurity-containing compounds in the anode metal. Thus, Ag, Se, and Te, present in the copper anodes, form refractory selenides and tellurides of Ag and Cu. Silver, present in the anodes, tends to plate on cathodes. The dissolution of silver is circumvented by maintaining a chloride level of 30 ppm in the copper refining electrolyte so that the silver ion concentration will not exceed the solubility product of AgCl. Nickel, present in the copper anodes, forms a refractory NiO, and ends up partially in the anode slime. In sulfate containing electrolytes, lead forms insoluble PbSO₄. When impurities from the anode become a problem, as in the case of nickel refining, a diaphragm separates the anode and cathode compartments. In electrowinning operations with insoluble anodes, it is not possible to eliminate noble metal impurities. Therefore, the electrolyte is treated to remove these impurities by cementation with active nickel powder in nickel electrowinning and with zinc powder in zinc electrowinning operations.

Selectivity of the cathodic process, with respect to the soluble impurities in electrorefining and electrowinning, is better with reversible metals such as Ag, Cu, Pb, and Zn than with nickel. Thus, electrorefined copper contains < 5 ppm Ni and < 1 ppm As and Sb, although they are present in relatively high concentrations in the refining electrolyte (~ 20 g/l Ni, ~ 1 g/l As, ~ 0.1 g/l Sb). Similarly, high purity silver can be deposited from solutions with ~1 g/l Cu and Pd, and high-purity zinc is produced from solutions containing ~ 1g/l Mn. However, in the case of nickel, soluble anode metal impurities (Cu, Fe, Co, Zn, Pb, As) are readily co-deposited. It should be noted that the most frequent cause of cathode contamination is the mechanical occlusion of anode slime, especially when the cathode is rough and porous. An example of this effect is the presence of > 20ppm Pb in electrorefined copper.

In electrowinning and electrorefining operations, thick metal deposits are grown over a period of several days (15 to 30, depending on the metal) and it is essential these be smoothed out without any dendritic growth or porosity. This is achieved by the use of addition agents. In copper refining, animal glue is used by most refineries, the typical addition rates being 3–100 g/ton of cathode weight. Other additives used in copper refining include thiourea, lignin related additives, avitone, safranin, and casein. Addition agents used in zinc electrowinning are: sodium silicate, gum Arabic, glue, cresylic acid, and a soya bean extract. Copper electrowinning operations often use guar gum—a natural colloid.

The relatively slow mass-transfer rates in the electrorefining and electrowinning operations present unique problems not encountered in other process industries.²⁹ For example, an average copper refinery, producing 500 tons Cu/day needs $\sim 0.2 \text{ km}^2$ of electrode area. This corresponds to 50,000 anodes and 50,000 cathodes suspended in 1500 tanks, occupying a total floor area of 6000 m^2 . A tank house is the heart of these operations regardless of the metal produced. The unique technological problems result from the fact that each of the many cells should be provided with a continuous supply of fresh electrolyte, continuous withdrawal of spent electrolyte, supply of electrical energy to the anodes and cathodes, periodic supply of new cathode blanks, removal of finished cathodes, and supply of soluble anodes, and periodic removal of anode slime.

The technological principles to achieve these needs are similar in the various refining and electrowinning operations as follows:

- (a) *Anodes.* The soluble anodes cast from the impure metal are usually 80–100 cm wide, 90–110 cm long, and 3–6 cm thick, depending on the anode life cycle and operating current density. They are continuously cast using automated equipment developed by some industries, such as Mitsubishi, Outokumpu, and some other companies. The anodes used in electrowinning from sulfate solutions are usually made of lead alloys. Zinc electrowinning anodes are Pb-Ag alloys containing 0.5 % Ag and 0.5 % Pb. Anodes made of Sb are used for copper electrowinning. Coated titanium anodes are not widely used for electrowinning because of the high cost of the oxygen evolving dimensionally stable anodes (DSA's), although they are used in some small electrolytic cells for electrowinning of Co and Ni.
- (b) *Cathodes.* Two types of cathodes are used for the electrodeposition of metals: reusable cathode blanks and sacrificial starter sheets. The reusable blanks, used in the zinc and cobalt electrowinning industry, are aluminum and stainless steel, respectively. Other electrowinning and refining operations use starter sheets, prepared by deposition on copper, stainless steel, or titanium blanks for ~ 24 hrs in a separate section of the tank house. Starter sheets are stripped from the blanks manually or by automatic stripping machines and prepared for use in the cells. Most of these operations are presently automated.

- (c) *Electrical circuits.* The most important aspect of the electrical circuitry in these operations is ensuring that all cathodes receive the same and uniform current density. This is achieved by using high quality anodes and cathodes, uniform electrode spacing, clean contacts, and suitable electrolyte composition having high throwing power.
- (d) *Electrolyte circulation.* In refining cells, electrolyte circulation is needed to provide a constant supply of addition agents, maintain a constant temperature and to ensure proper composition by removing the soluble impurities. Copper refining operations circulate the electrolyte through steam heat exchangers and addition agent feed tanks at 20–40 l/m per cell. A small part of this stream is treated to remove soluble impurities such as Ni, As, and Sb. Soluble impurities in nickel-refining are removed from the common anode compartment, purified and returned to the cathodes boxes of the Hybinette cells. In electrowinning operations, electrolyte circulation ensures a constant metal ion concentration in the cathode compartment. Transferring the spent electrolyte to the chemical replenishing operation and returning it as pregnant electrolyte achieves this requirement.
- (e) *Slime handling.* In copper and nickel-refining cells, the anode slimes from the dissolving anodes are accumulated at the cell bottom. They are removed either manually or by submerged “vacuum cleaners”. The anode slimes in lead and nickel refining, with a sulfide anode, remain on the anode and are removed with a slime removal machine with water spray and rotating brushes.
- (f) *Material handling.* A 500 tons/day copper refinery typically handles about 2000 new cathodes, 2000 spent anodes, 4000 starter sheets, and 4000 finished cathodes. Because of the large number of electrodes involved in these operations, efficient material handling systems are required. These operations are presently automated.
- (g) *Electrolyte mist in electrowinning.* Oxygen generated at the anodes forms a fine mist of electrolyte and makes the tank house atmosphere unhealthy. The maximum mist content is set by some local authorities to ~ 1mg of major electrolyte component (e.g., H_2SO_4) per 1 m^3 of air above the cells. While some copper electrowinning operations use frothing agents such as Dowfax 2AO, some use several layers of plastic balls to suppress the mist. Nickel and zinc electrowinning circuits use forced ventilation systems or properly ventilated hoods.

Figure 3.14 shows a schematic of a typical electrorefining operation. Table 3.12 depicts the operating conditions⁵ for the electrorefining of Cu, Ni, Pb, Co, and Sn, and Table 3.13 describes the components of cell voltage for the refining and electrowinning of Cu, Ni, and Zn.

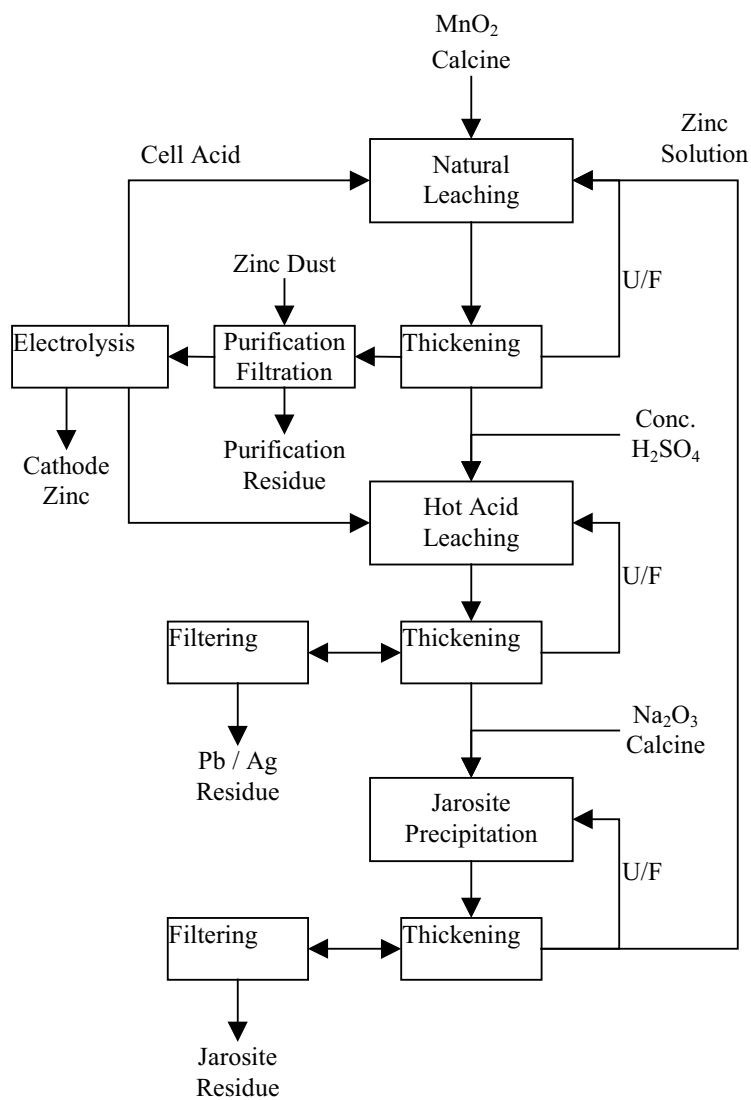


Figure 3.14. Typical leaching-jarosite precipitation flow sheet. Reprinted from Reference 29.

TABLE 3.12
Operating Parameters for Electrefining of Metals

Metal	Concentration g/dm ³	Current density mA/cm ²	Cell Voltage V	Temperature °C	Current efficiency %		Impurities	
							slime	solution
Copper	CuSO ₄ (100-140) H ₂ SO ₄ (180-250)	10-20	0.15-0.30	60	95		Ag, Au, Ni, Pb, Sb	Ni, As, Fe, Co
Nickel	NiSO ₄ (140-160) NaCl (100) H ₃ BO ₃ (10-20)	15-20	1.5-3.0	60	98		Ag, Au, Pt	Cu, Co
Cobalt	CoSO ₄ (150-160) Na ₂ SO ₄ (120-140) NaCl (15-20) H ₃ BO ₃ (10-20)	15-20	1.5-3.0	60	75-85		---	Ni, Cu
Lead	Pb ²⁺ (60-80) H ₂ SiF ₆ (50-100)	15-25	0.3-0.6	30-50	95		Bi, Ag, Au, Sb	---
Tin	Na ₂ SnO ₃ (40-80) NaOH (8-20)	5-15	0.3-0.6	20-60	65		Pb, Sb	---

TABLE 3.13
Typical Energy Requirements in Electrorefining and Electrowinning

	Copper		Nickel refining		Zinc
	Refining	Winning	Metal anode	Sulfide anode	electrowinning
Current density, kA/m^2	2.1	3	2	2	5.7
Current efficiency, %	97	85	96	96	90
Cell voltage, V	0.28	2.0	1.9	3.7	3.5
Reversible cell potential, V	0	0.9	0	0.35	2.0
Cathode overpotential, V	0.08	0.05	0.25	1.5	0.15
Anode overpotential, V	0.03	0.6	0.3	0.25	0.6
Ohmic drops, IR , V	0.1	0.4	1.05*	1.25*	0.5
Cell hardware, IR , V	0.07	0.5	0.3	0.35	0.25
Energy consumption, kW h/kg	0.25	2	1.9	3.5	3.3

*with diaphragm

TABLE 3.14
Breakdown of Capital Costs for Electrorefining

	\$ per annual ton
Anode weighing, straightening, lug milling, sampling equipment	50
Electrolysis equipment, includes transformers, rectifiers, cells	250
Electrolyte purification and circulation equipment	100
Cathode preparation equipment	25
Materials handling and anode casting equipment	75
Total	500

TABLE 3.15
Breakdown of Capital Costs for Cu Electrowinning*

	\$ per annual ton of Cu
Leach heap pad, piping, pumps, collection ponds, etc.	270
Solvent extraction plant	310
Electrowinning plant	250
Pb-Sn-Ca anodes	50
Stainless steel mother blank cathodes	60
Cranes and other moving equipment	10
Cathode handling equipment	70
Control system for solvent extraction and electrowinning plants	50
Engineering services, contingency, etc.	370
Total	1440

*by the heap leach/solvent extraction/electrowinning route

3.5.3. Economics

The capital costs vary significantly for different mining operations because of differences in ore grades, mining methods, ground conditions, and mine sizes. The costs provided in this Chapter are approximate and are based on several assumptions. Typically, the capital cost³⁰ of a new copper refinery, in 1993 dollars, is about \$500/annual ton of electrorefined cathodes, whereas the capital cost for a heap leach/solvent extraction and electrowinning plant is \$1440/annual ton of copper. The breakdown of these costs is presented in Tables 3.14 and 3.15. The direct operating costs for producing electrorefined cathode are \$0.10 per kg of copper, of which 20% is for electricity, 40% for manpower, 25% for maintenance materials, and the rest for overheads. The breakdown of the copper electrowinning costs is presented in Table 3.16.

The capital costs³¹ for zinc production are \$2500/annual ton for production levels of 100,00 tons/year, while the operating costs are \$0.45–\$0.70/kg of zinc. The electricity cost is about 34% of the operating cost, while labor accounts for 32% and others constitute the rest.

TABLE 3.16
Breakdown of Operating Costs for Cu electrowinning*

	\$ per kg of Cu
Heap operation and maintenance	0.09
Sulfuric acid	0.03
Solvent-extraction plant operation and maintenance	0.03
Reagent make-up	0.04
Electrowinning-tankhouse operations, includes electrical energy and maintenance	0.13
Overheads	0.05
Total	0.37

*by the heap leach/solvent extraction/electrowinning route

3.5.4. Benefits to or from Fuel Cell Technology

Table 3.17 shows the process energy (PE) requirements to produce Al, Cu, Zn, Mg, and Ni. These PE values are expressed as total kJ equivalents of primary fuel requirements to make these metals and include the fuel requirements for mining, crushing, processing, production of reagents, and for the electricity consumed. Electricity is assumed to be produced in a fossil fuel-fired power plant at an average conversion efficiency of 32%, which corresponds to 11,100 kJ of primary fuel per kWh. It is interesting to note that the electric energy usage for electrolysis is significant for Al and Zn, whereas copper requires a small fraction of the PE. Therefore, the price of aluminum is more sensitive to the cost of energy when compared to the other metals. However, declining grades of available ores for Cu, Zn, and other metals will increase the overall PE, and thus the selling price will be dictated by the cost of energy. A comparison of the PE values³² with the theoretically needed chemical energy to convert the ore into metal shows (see

Table 3.17
Energy Use in Electrometallurgy

Metal	Total PE MM kJ/ton	Energy use in electrolysis	
		Electrolysis	Others
Al	284	195	33
Cu	130	3	3
Zn	70	44	1
Mg	308	186	5
Ni	167	20	7

TABLE 3.18
Comparison of Process Energy (PE) and Free Energy

Reaction	Energy (MM kJ/ton of metal)	
	ΔG^* at 25 °C	PE
$2 \text{ Al}_2\text{O}_3 \cdot \text{H}_2\text{O} + 3 \text{ C} \rightarrow 4 \text{ Al} + 3 \text{ CO}_2 + 2 \text{ H}_2\text{O}$	19	284
$2 \text{ CuFeS}_2 + 5 \text{ O}_2 + \text{ SiO}_2 \rightarrow 2 \text{ Cu} + 4 \text{ SO}_2 + 2 \text{ FeO} \cdot \text{SiO}_2$	-11	130
$\text{ZnS} + \text{O}_2 \rightarrow \text{Zn} + \text{SO}_2$	- 1.5	70

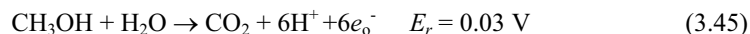
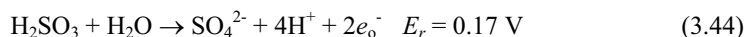
* ΔG refers to the free energy change of the reaction.

Table 3.18) that the chemical energy is less than 10% of PE for Al and is negative (energy released) for Cu and Zn. The large PE values are a consequence of the separation technologies required for processing the ore to make the electrolyte for electrolysis. Therefore, there is a significant opportunity to reduce the overall energy requirements by developing new technologies not only for electrolysis, but also for pre-electrolysis steps.

A significant portion of the cell voltage of Zn, Cu, Ni, and Co electrowinning cells is the reversible voltage of the oxygen evolution reaction and the overpotential associated with it:



Various alternate half-cell reactions, examined in an attempt to lower the overall energy consumption for the production of these metals, are:



The cuprous/cupric chloride anode reaction is commercially practiced in the Duval electrowinning process. It is economical as it combines the low half-cell potential with one electron participation. This anode reaction, in addition to lowering the cell voltage, also regenerates CuCl^+ used in the process. The cell voltage of this electrowinning process is 1 kWh/kg of copper. Reactions (3.42) to (3.46) have been extensively studied to replace the oxygen evolution reaction. While this approach is theoretically attractive, none of them have become

commercial as yet. Slow kinetics of reaction (cf. reaction 3.43) and poor cathode efficiency, because of the reduction of Fe^{3+} during the reaction, were attributed as reasons for abandoning these two schemes. The energy savings with the other schemes appear to be relatively modest compared to the costs and operating problems associated with implementing these alternate anode reactions. It is important to note that studies with the hydrogen depolarized anode have shown a cell voltage lowering from 3.5 V to 1.55 V at 150 A/m^2 , a reduction of 65% in energy savings for the zinc electrowinning process.³³

3.6. CORROSION INHIBITION/PASSIVATION

3.6.1. Background

Corrosion of materials in buildings bridges, automobiles, ships, pipelines, etc. is very extensive and the expenses incurred in replacing these materials and in methods used to inhibit corrosion, including passivation, are enormous. In several countries these account for a few percent of the Gross National Product. In the USA, this expense is over \$300 billion. An understanding of these phenomena and their technologies is most essential in fuel-cell research and development. Stability of the component materials for a fuel-cell power plant, from the single cell to the stack level, is vital for the attainment of the desired lifetimes. For the power generation application, the goal set for the operating lifetime of the electrochemical cell stack by the US Department of Energy is 40,000 h; for the transportation application it is about 3000 h, over a period of 5 years; and for the portable power it is in the range of 1000 to 10,000 h. The problem of corrosion is encountered in fuel cells because of the attack of electrodes and current collectors by the acidic, alkaline, or molten carbonate electrolytes, particularly in the oxidizing environment of the oxygen electrode. Even in the solid oxide fuel cells, corrosion problems are encountered.

There are excellent books, chapters in books, review articles, and original papers in journals about the topics of corrosion inhibition and passivation. To be more specific, the reader is referred to *Corrosion Engineering* by Green and Fontana; *Handbook of Corrosion* by Uhlig; *Handbook of Corrosion Engineering* by Roberge; Chapter 8 in the book *Surface Electrochemistry—A Molecular Level Approach* by Bockris and Khan; and a section of a chapter in *Electrochemistry* by Rieger.³⁴

Within the limited space available for this Section, we shall deal with (i) the principles of the technologies dealing with corrosion inhibition and passivation and (ii) the benefits to and from fuel cell technologies. The economic aspects and other applications are dealt in the above-mentioned references in great detail.

3.6.2. Principles of Technologies

Corrosion is caused by the oxidation of metal. The cathodic reaction in the oxidation of a metal, like iron, is:



while the anodic reaction is either reduction of oxygen,



or the evolution of hydrogen:



The rates of these reactions are dependent on the environment that the metallic elements are exposed to. The pH of the medium and the oxygen concentration in the environment also have strong influences on the corrosion rate. The presence of halide (mostly chloride) ions accelerates the corrosion rate.

A most valuable method of assessing the stability of materials is by using Pourbaix diagrams. It presents a thermodynamic perspective of the stabilities of the metals and their oxides as a function of potential and of pH. A potential vs. pH diagram (Pourbaix diagram) for iron is illustrated in Figure 3.15. This figure shows the region of stability of the metal and its oxides as a function of the potential and

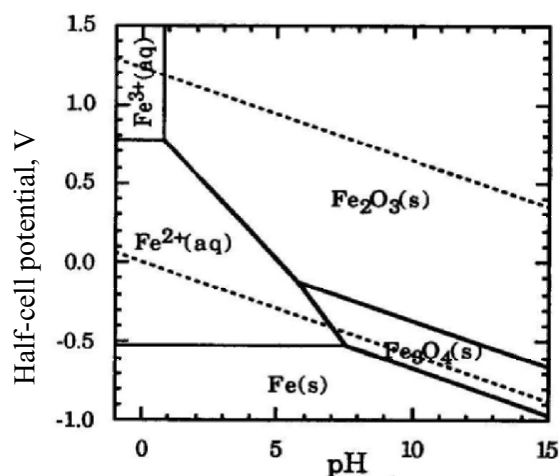


Figure 3.15. Potential vs pH diagram (Pourbaix diagram) for iron. Reproduced with permission from Reference 34.

the pH. To construct these diagrams, arbitrary values are assumed for the metal-ion concentration (10^{-6} m/l) and the pressures of oxygen and hydrogen (1 atm). There will be a shift in these curves with the variations of these concentrations.

The corrosion rates, however, depend on the kinetics of the metal dissolution reaction and the rates of either the hydrogen evolution or oxygen reduction. If the reversible potential for the metal dissolution reaction is considerably more cathodic than that for the hydrogen evolution reaction, the anodic reaction becomes dominant. The reaction rate also depends on the pH of the liquid medium that the metal or alloy is exposed to. Most metals are stable at higher pH. But then, there is a take-over by the oxygen reduction as the cathodic reaction and corrosion of the metal or alloy will still occur.

As stated in Chapter 1 Section 1.3, a *mixed potential* is set up when corrosion occurs. At this potential, the rate of metal dissolution is equal to the rate of the oxygen reduction. The mixed potential (V_{corr}) is expressed by the equation:

$$V_{corr} = \frac{RT}{F} \ln \left\{ \frac{i_{O,H} \exp\left(\frac{V_{r,H}F}{2RT}\right) + i_{O,M} \exp\left(\frac{V_{r,M}F}{2RT}\right)}{i_{O,H} \exp\left(\frac{-V_{r,H}F}{2RT}\right) + i_{O,M} \exp\left(\frac{-V_{r,M}F}{2RT}\right)} \right\} \quad (3.50)$$

where $i_{O,H}$ and $i_{O,M}$ are the exchange current densities for the hydrogen evolution and metal dissolution reaction, respectively, $V_{r,H}$ and $V_{r,M}$ are the reversible potentials for these reactions, and the transfer coefficient (α) of both the reactions is assumed to be $\frac{1}{2}$. The corrosion current density is expressed by the equation:

$$i_{corr} = i_{O,M} \left\{ \frac{\left[i_{O,H} \exp\left(\frac{-V_{r,H}F}{2RT}\right) + i_{O,M} \exp\left(\frac{[V_{r,M} - V_{r,H}]F}{2RT}\right) \right]^{-\frac{1}{2}}}{\left[i_{O,H} \exp\left(\frac{-V_{r,H}F}{2RT}\right) + i_{O,M} \exp\left(\frac{-V_{r,M}F}{2RT}\right) \right]} - \frac{\left[i_{O,H} \exp\left(\frac{-V_{r,H}F}{2RT}\right) + i_{O,M} \exp\left(\frac{[V_{r,M} - V_{r,H}]F}{2RT}\right) \right]^{\frac{1}{2}}}{\left[i_{O,H} \exp\left(\frac{-V_{r,H}F}{2RT}\right) + i_{O,M} \exp\left(\frac{-V_{r,M}F}{2RT}\right) \right]} \right\} \quad (3.51)$$

It is only when $V_{r,H} > V_{r,M}$ that i_{corr} is positive.

From an experimental point of view, it is simple to measure the corrosion potentials and the corrosion current densities. One may use either the linear polarization method or the extrapolation of the Tafel lines for the anodic and cathodic reactions. A third method is to use electrochemical impedance spectroscopy (see Chapter 6).

For corrosion inhibition, several procedures have been employed. One method is by *cathodic protection*—i.e., making the potential of the method more negative by passing a small current between the metal and an auxiliary electrode. Another method is to use a metal with a more negative reversible potential (e.g., zinc) as the counter electrode (*sacrificial anode*) and connecting the two electrodes, as in a galvanic cell. This method is widely used for corrosion protection of bridges on roads and on railway lines and of ships. A second method of corrosion inhibition is by use of *protective coatings*—e.g., paints, plastics, ceramics, or coating of a metal like nickel or chromium, which form insulating oxides or gold films, which are quite stable. A third method is by using organic compounds that adsorb strongly on the metal. These *inhibitors* have the advantages of being able to greatly reduce the rates of the metal dissolution, oxygen reduction, and hydrogen evolution reaction. Typical inhibitors are aliphatic or aromatic amines. Only small quantities of the inhibitor are necessary.

Passivation of metals is another important electrochemical phenomena. It occurs on metals or alloys that form stable oxides on the surface. In most cases, these oxides are insulators, but in some cases, even if these passive layers are electronically conducting, they prevent the dissolution of the metallic substrate. The passivation of a metal can best be illustrated by the potential vs. current density plot on a metal, when it is polarized anodically (Figure 3.16). As the potential increases, the current increases due to metal dissolution. A further increase of potential then causes a sharp decrease in the current density due to the formation of a stable oxide film. The potential at which the current starts to decrease is referred to as the Flade potential. There is then an appreciable region of potential when the current has a low constant value—the passivation region. A still further increase of potential causes a fairly rapid increase of the current—i.e., in the transpassive region. This is effectively caused by the passive oxide layer transforming to a higher oxide that is ionically conducting (sometimes even electronically conducting). This type of behavior typically occurs with some transition metal oxides—e.g., cobalt, nickel, chromium.

3.6.3. Benefits to or from Fuel Cell Technologies

The competing reactions, which occur during corrosion of a metal are either/both the hydrogen evolution and oxygen reduction reactions. An understanding of the mechanism and kinetics of these reactions in Fuel Cell R&D can be beneficial to inhibit corrosion. For example, carbon monoxide and sulfur species inhibit the hydrogen oxidation reaction. Organic impurities also greatly slow

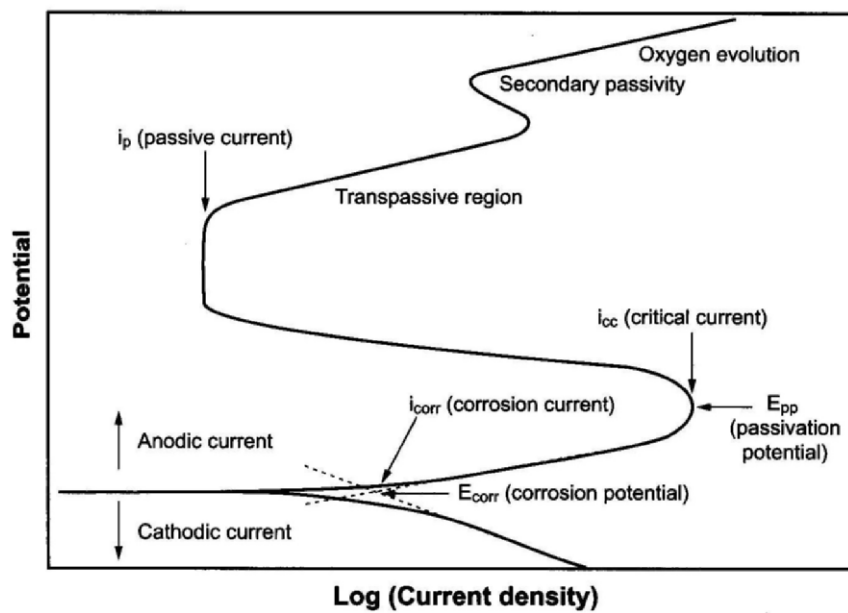


Figure 3.16. Typical potential vs current density plot for a metal or alloy exhibiting the corrosion, passivation and transpassive regions – arbitrary units. Reprinted from Reference 35, Copyright (1999) with permission from The McGraw-Hill Companies.

down the kinetics of the oxygen reduction reaction. The evaluation of these types of species in corrosion inhibition may be valuable.

One problem encountered in electrochemical-cell stacks is corrosion or passivation of metallic bipolar plates (e.g., steel in the former case or aluminum in the latter case). Gold-plating of these metallic elements has been evaluated. This procedure may be too expensive for the large-scale manufacture of fuel cells. Furthermore, if there are micropores in the gold film, local corrosion of the substrate could occur. An alternative is to use graphite with a binder for coating of these bipolar plates. One other problem found in fuel cells is the slow corrosion of the carbon support in the low and intermediate temperature fuel cells (e.g., PEMFC, AFC, PAFC). The corrosion rate is higher when the potentials of the oxygen electrode are closer to the open circuit potential. Several methods have been examined to reduce the corrosion rate—e.g., high temperature heat treatment to graphitize the carbon or treatment with nitric acid. It may be worthwhile using the former method for corrosion inhibition.

3.7. ELECTROCHEMICAL-ENERGY STORAGE

3.7.1. Background

Basically, there are two types of electrochemical-energy storage technologies: batteries and electrochemical capacitors. The common feature of both these technologies is that chemical energy is directly converted into electricity, just as in the case of fuel cells. The main difference between electrochemical-energy conversion (fuel cells) and electrochemical energy (batteries and electrochemical capacitors) is that in the former the oxidant and the reductant are fed into the electrochemical cell stack, while in the latter, both the reactants are in a sealed container, with a separator keeping the oxidant and the reductant apart. The distinctive features of both of these technologies are dealt with in Chapter 4, Section 4.2.

The battery technology is one of the oldest electrochemical technologies and dates back to the middle of the 19th century. Lead acid batteries had reached the commercialization stage in the latter part of this century. Batteries could be subdivided into four types:

- primary,
- secondary,
- reserve, and
- thermal batteries.

In this chapter we shall focus on the first two types. Short descriptions will be made on the other two types. As in all electrochemical cells, batteries (as well as capacitors) contain an anode, a cathode, and an electrolyte, with a separator containing the electrolyte between the anode and cathode to prevent the transport of the active materials (oxidant and reductant) from one electrode to the other. In essence, a battery is a galvanic cell, and it is desirable to have a high thermodynamic reversible potential. When power is needed from the battery, it is connected to an external load. The main difference between a primary and secondary battery is that in the former, it is the desired amount of chemical energy (and hence, the resultant electrical energy) that is stored in the active materials. In a secondary battery, once the oxidant and reductant of the active materials are depleted, their activities can be regenerated by charging the batteries with electrical energy.

Electrochemical capacitors are similar to secondary batteries (rechargeable). The main difference is that the amount of electric energy storage is considerably less than in secondary batteries. Electrochemical capacitors have the advantage of attaining very high rates of delivery of electrical power.

There are a multitude of types of primary and secondary batteries and probably several million publications on these technologies. One of the most valuable publications is the *Handbook of Batteries*,³⁶ which provides a comprehensive survey of all types of batteries. Within the space allocated for this Section, only a

TABLE 3.19
Types of Batteries, Selected for Brief Analysis in Section 3.7

Primary	Secondary	Reserve
Zinc/Manganese	Lead Acid	Magnesium-water activated
Zinc/Air	Nickel/Hydrogen	
Lithium/Thionyl Chloride	Nickel/Cadmium	
	Nickel/Metal	
	Hydride	
	Lithium/Ion	

small fraction of these technologies is summarized. Table 3.19 presents the types of batteries chosen for this brief analysis. The main reason for their selection is that these types of batteries are relevant to fuel cells, in respect to technical, competing and synergistic (hybrid fuel cell/batteries) aspects. Section 3.7.6 is devoted to electrochemical capacitors.

According to a recent review,⁷ the worldwide sales of batteries amounted to \$39 billion in 2001; two thirds of this amount were from secondary batteries. Some interesting techno-economic aspects of the batteries chosen for the description in this chapter are found in Table 3.20.

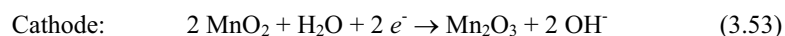
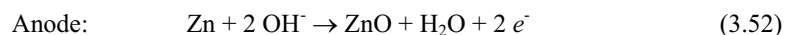
TABLE 3.20
Some Techno-Economic Aspects of Primary and Secondary Batteries.

Type of battery	Operating temperature (°C)	Cycle life	Cost (\$/kW/h)	Worldwide sales (million \$), (manufacturer's cost)
Primary				
Zn/MnO ₂	0 – 50	N/A	1000	
Secondary				
Lead Acid	-40 – 50	200 – 1500	200	13,000
Alkaline Ni (Negative electrode Cd, MH)	-20 – 50	300 – 600	400	3,500
Lithium-Ion	-20 – 40	>1000	800	2,500

3.7.2. Primary Batteries

3.7.2.1. Zinc/Manganese Dioxide.

- (a) *Background.* Historically, the Leclanche cell, based on zinc-manganese dioxide, was first invented. It had the active materials, separated by a gel electrolyte, containing ammonium chloride as the electrolyte. Since the 1950s, the most commercialized zinc-manganese dioxide batteries have an alkaline electrolyte. These batteries contain electrolytically produced manganese dioxide (positive electrode), the needed polymer gelling agents for the potassium hydroxide electrolyte (8 M KOH) and powdered zinc for the negative electrode.
- (b) *Principles of technology.* The overall reaction, the standard thermodynamic reversible potential, the specific energy and energy density of alkaline Zn-MnO₂ batteries, along with those for the other batteries considered in this Chapter, are tabulated in Table 3.21. The half cell reactions are as follows:



The cathode material generally contains manganese dioxide powder (70 to 80%), graphite powder (7 to 10%) and acetylene black (1 to 3%). The carbon materials enhanced the electronic conductivity of the electrodes. Binder materials (6% Portland cement and fibers) are included for mechanical strength. The separator material (in gel form, e.g., carboxymethylcellulose) has two functions—one to have good absorption of the KOH electrolyte for high ionic conductivity and the other to prevent zinc penetration. The zinc powder is contained in a polymer gel.

In respect to the design of the battery, the most common is the cylindrical one (types A, AA, AAA, B, C, D). Figure 3.17 illustrated in a review by Kordesch, is reproduced in this Chapter. These batteries have an open circuit potential of about 1.5 V, which is close to the reversible potential. The capacity is generally about 10 Ah for the D size battery. The other type of design is the prismatic one (Figure 3.18). A large percentage of batteries with this design have an open circuit potential of 9 V, which means that six cells are connected in series externally (a unipolar design). Typical *discharge plots* (cell potential–time plots) for the AA-cells under low and high rates of discharge are illustrated in Figure 3.19.

- (c) *Economics and applications.* The Zn-MnO₂ battery is a relatively inexpensive one and is the most widely used primary battery. However, the cost of these batteries as a function of their energy is high (\$1/Wh),

TABLE 3.21.
Performance Characteristics of the Selected Batteries for Brief Analysis in this Chapter

Type of battery	Cell reaction	Standard thermodynamic reversible potential, V	Specific energy (attained), Wh/kg	Energy density (attained), Wh/l
Primary				
Zn-MnO ₂	$\text{Zn} + 2 \text{MnO}_2 \rightarrow \text{ZnO} + \text{Mn}_2\text{O}_3$	1.5	145	400
Zn-Air	$\text{Zn} + \frac{1}{2} \text{O}_2 \rightarrow \text{ZnO}$	1.65	370	1300
Li-SOCl ₂	$4 \text{Li} + 2 \text{SOCl}_2 \rightarrow 4 \text{LiCl} + \text{S} + \text{SO}_2$	3.65	590	1300
Secondary				
Lead Acid	$\text{Pb} + \text{PbO}_2 + 2 \text{H}_2\text{SO}_4 \rightarrow 2 \text{PbSO}_4 + 2 \text{H}_2\text{O}$	2.1	35	70
Ni-H ₂	$\text{H}_2 + 2 \text{NiOOH} \rightarrow 2 \text{Ni(OH)}_2$	1.5	55	60
Ni-Cd	$\text{Cd} + 2 \text{NiOOH} \rightarrow 2 \text{Ni(OH)}_2 + \text{Cd(OH)}_2$	1.35	35	100
Ni-MH	$\text{MH} + \text{NiOOH} \rightarrow \text{M} + \text{Ni(OH)}_2$	1.35	75	240
Lithium Ion	$\text{Li}_x\text{C}_6 + \text{Li}_{1-x}\text{CoO}_2 \rightarrow \text{LiCoO}_2 + \text{C}_6$	4.1	150	400
Reserve				
Mg-water activated	$\text{Mg} + 2\text{AgCl} \rightarrow \text{MgCl}_2 + 2\text{Ag}$	1.4 – 1.6	130	200

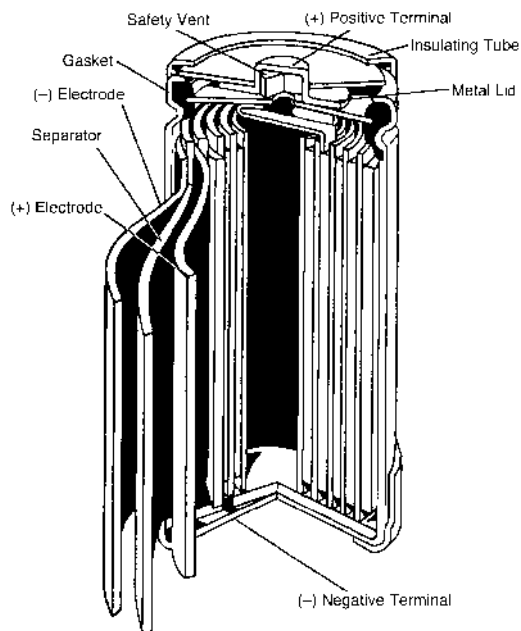


Figure 3.17. Schematic of a cylindrical design for a battery; this design is similar for primary and secondary batteries. Reprinted from Reference 36, Copyright (2002) with permission from The McGraw-Hill Companies.³⁶

and they generally have rather low capacities. These batteries have a wide variety of applications (motor toys, intermittent lighting, radios, power-packs for soldiers, etc.). But due to their short lifetimes, there is interest in making these rechargeable and such types have reached the commercialization stage. There is also competition from primary lithium and zinc/air batteries for these applications.

- (d) *Benefits to or from fuel-cell technologies.* At the present time, there is no benefit to or from fuel cell technologies from Zn/MnO₂ batteries. But it is worthwhile mentioning that for military applications (power-packs for soldiers), there is some interest in replacing these batteries with PEMFCs and DMFCs because of the considerably higher energy densities for the two latter type of batteries than that for the former.

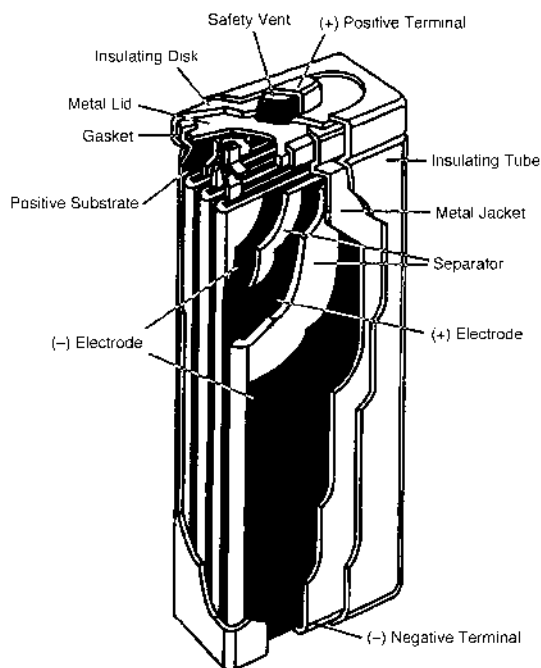


Figure 3.18. Schematics of a prismatic design for a battery. This design is similar for primary and secondary batteries. Reproduced from Reference 36, Copyright (2002), with permission of The McGraw-Hill Companies.

3.7.2.2. Zinc/Air

- (a) *Background.* The most advanced of the metal-air batteries is the one with air for the positive electrode (as in the case of a fuel cell) and with zinc for the negative electrode. The second most advanced one is the aluminum-air battery. These batteries are attractive because they have relatively high energy densities.
- (b) *Principles of technology.* A zinc/air battery contains a positive air electrode and a negative zinc electrode and an alkaline electrolyte (8 M KOH). The electrooxidation of zinc occurs according to the electrochemical reaction as represented by Eq. (3.52). The oxygen reduction reaction is the same as that in an alkaline fuel cell, i.e.,

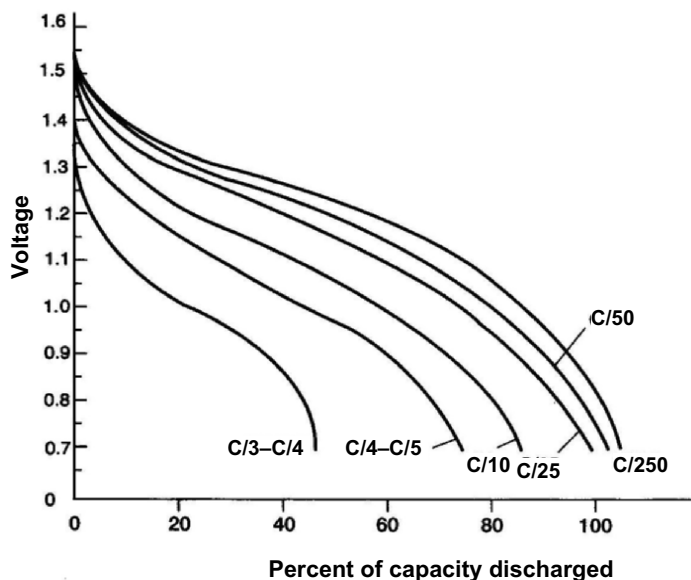


Figure 3.19. Typical discharge plots for an AA Zn/MnO₂ battery under different rates of discharge. Discharge rates are expressed as a fraction of C, defined as the discharge current in amps divided by the rated capacity of the battery in amp-hour. Reproduced from Reference 36, Copyright (2002), with permission of The McGraw-Hill Companies.



High surface area carbon has most widely been used as the electrocatalyst for oxygen reduction. But at this electrocatalyst, the predominant reaction leads to hydrogen peroxide, as represented by,



The coulombic efficiency for this reaction is half that for oxygen reduction. Thus, in recent times, there has been a trend towards using high surface area platinum supported on high surface area carbon as the electrocatalyst. The electrocatalyst loading can be as low as 0.2 mg/cm². Alternative electrocatalysts that give a high performance are heat-treated organic macrocyclics (e.g., cobalt tetraphenyl porphyrin) and high surface area nickel-cobalt spinels.

In the original zinc-air cells, a large plate of amalgamated zinc was used for the negative electrode. Presently, the anode consists of zinc

powder, potassium hydroxide contained in a polymeric gel, and a current collector. Initially, carbon plates were used for the cathode but currently with the advances in fuel cell technology, porous gas diffusion electrodes, as in alkaline fuel cells, are used. For the current collector, a metallic grid is used. A multi-layer polymeric absorbent is used for the separator containing the electrolyte. On the outer surface of the air electrode, a thin polymeric layer is formed to inhibit the transport of carbon dioxide and water into the cells. Original zinc/air cells contained a complex manifold and internal structure for airflow. An essential criterion in the design of the battery is to optimize the flow of air into the porous gas-diffusion cathode. In the miniature cells, the bottom of the container has air inlet holes.

An innovative design was researched for a zinc/air battery by Appleby, Jacqueline, and Pompon.³⁷ Powdered zinc, contained in the circulating electrolyte, was fed to a cell with a tubular design. The inner wall of the metallic tube served as the current collector for the zinc electrode. The outer wall contained a separator material and the air electrode. Thus, this cell functioned very much like a fuel cell with the electric power being generated only when the reactants were delivered to the cell. The cell performed reasonably well. The tubes had a constant cross-section. The main overpotential losses were due to activation overpotential at the air electrode and ohmic resistance. One reason for the high ohmic resistance was the high contact resistance (electronic) of the slurry particles with the current collector. A bundle of tubes were connected in series and in parallel to attain the desired potentials of the cell stacks and total currents. It was proposed that the zinc oxide produced by the anodic reaction could be reduced externally (electrochemically or using thermal energy). Specific energy of 110 Wh/kg was obtained at the 3h discharge rate. The energy efficiency of the stack was relatively low (about 40%) because of high activation overpotential and ohmic overpotential losses.

- (c) *Applications and economics.* Historically, zinc/air batteries were first used as power sources for railway signal and warning devices. These were soon replaced by the better performing, more reliable, and long lifetime nickel-iron batteries. Since the mid-fifties, the main application of the zinc/air batteries has been for hearing aids. Button-type cells are used for this purpose. The tubular design zinc/air batteries were proposed as attractive batteries for electric vehicles. As stated in Principles and Technology of Zn-Air Batteries, the energy density and efficiency are far too low for this application. Aluminum/air batteries, with a higher energy density, have also been proposed for this application. On a \$/kWh basis, the costs for the portable electronic application is high (\approx \$1000/kWh), but it has been projected that for the automobile power application, the cost will be about \$400/kWh.

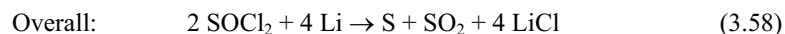
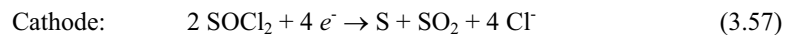
- (d) *Benefits to or from the fuel-cell program.* From the preceding description of this type of battery, what is most visible is that the development of highly efficient air electrodes for alkaline fuel cells has greatly benefited the state-of-the-art zinc/air batteries.

3.7.2.3. Lithium

- (a) *Background.* Lithium is the most positive element and it is the lightest of all metals. If it is coupled with fluorine, the most electronegative and the lightest of all the group VII elements in the chemical periodic table, this battery will exhibit the highest thermodynamic reversible potential, as well as the highest energy densities. It is practically impossible to develop a lithium battery in aqueous media because of its rapid reaction with water to produce hydrogen. Hence, these batteries have been developed using organic and solid electrolytes. These electrolytes have to be compatible with lithium for chemical stability. The commonly used electrolytes are the lithium salts of perchloric acid, hexafluorophosphoric acid, hexafluoroarsenic acid, tetrafluoroboric acid, and trifluoromethane sulfonic acid. These are dissolved in aprotic solvents such as ethylene carbonate, propylene carbonate (or sometimes the mixture of the two), dimethyl formamide, tetrahydrofuran, and several others. The cathode materials could be in the solid or liquid state. Examples of the former are carbon monofluoride, manganese dioxide, copper oxide, iron sulfide, and silver chromate. Figure 3.20 illustrates the significantly higher specific energies of some of these lithium batteries in comparison with the well-developed alkaline Zn/MnO₂ battery.

Primary lithium batteries have also been developed and commercialized with liquid cathodes. The most common liquid cathode cells use sulfur dioxide with thionyl chloride. The liquid cathodes also serve as the solvent. A third type of lithium battery has a solid electrolyte (e.g., lithium iodide) with an organic additive (e.g., polyvinyl pyridine). The electrolyte is mixed with the cathodic reactant (iodine) to form a charge transfer complex. For the purpose of this discussion of a primary lithium battery, we have chosen the lithium-thionyl chloride battery.

- (b) *Principles of technology.* The lithium-thionyl chloride battery has the highest energy density. The reactions occurring in the cell are:



In the negative electrode, a lithium sheet is pressed onto an expanded nickel screen, which serves as the current collector. The anode and

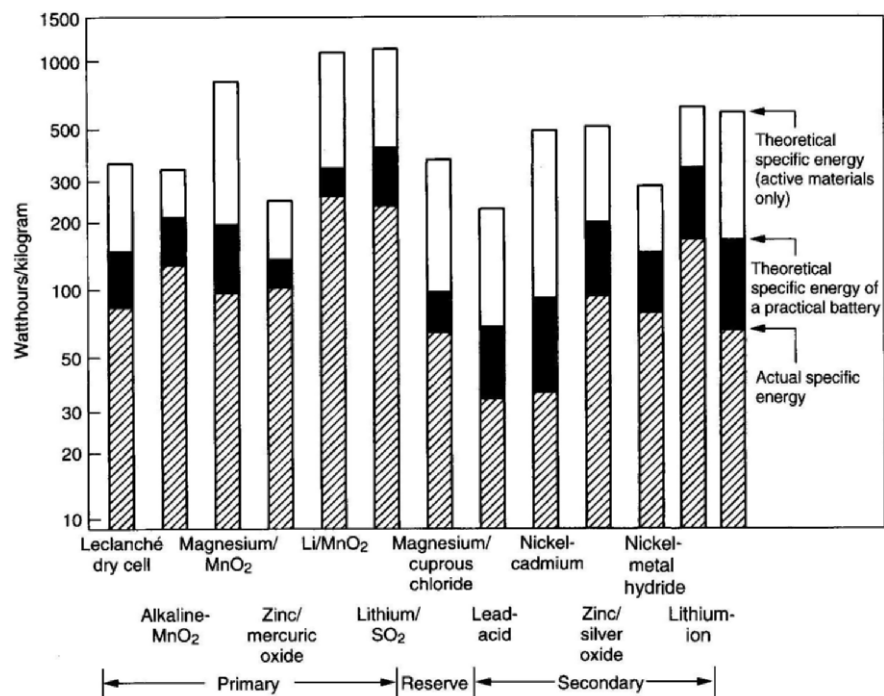


Figure 3.20. Specific energies for some primary, secondary, and reserve batteries. Reproduced from Reference 36, Copyright (2002), with permission of The McGraw-Hill Companies.

cathode are separated by glass filter papers; fluorocarbon plastics are used as insulators. In respect to the designs of the cells, the most common are the cylindrical cells (types AA, C, D as in the alkaline Zn/MnO₂ cells). For low capacity cells, bobbin and button type cells are used. It is interesting to compare the cell potential vs. capacity plots for typical Li/SOCl₂, Zn/MnO₂, and Zn/Air batteries (Figure 3.21). The significant advantage of the lithium battery is that its plateau potential is about 3.5 V, as compared with about 1.4 V for the Zn/MnO₂ battery.

There are safety measures that have to be taken into consideration in the manufacture of lithium batteries. Water impurities have to be completely avoided. The combination of SOCl₂ and water can produce hydrochloric acid and sulfuric acid. Direct contact of the anodic and cathodic reactants can lead to explosions.

- (c) *Applications and economics.* Because of the high energy densities and cell voltages, the US Department of Defense uses this type of battery for the

same applications as with Zn/MnO₂ batteries. Such batteries are also used in watches. The lithium batteries are at least five times as expensive as Zn/MnO₂ batteries on a \$/kWh basis.

- (d) *Benefits to or from fuel-cell technologies.* Since these batteries are of the non-aqueous type, there is no common feature in its development with fuel cell technologies. One noteworthy mention is that for some portable applications, the lithium batteries have an advantage over fuel cells because each cell has an operating potential of over five times as that of a hydrogen/air fuel cell.

3.7.3. Secondary Batteries

3.7.3.1. Lead Acid

- (a) *Background.* The lead acid battery is the oldest and most commercialized of all types of batteries. Plante invented it in 1859. Its most widespread application is as a starter battery for transportation vehicles.
- (b) *Principles of technology.* The overall reaction in a lead acid battery and the standard thermodynamic reversible potential are as stated in Table 3.21. The half cell reactions are expressed by:

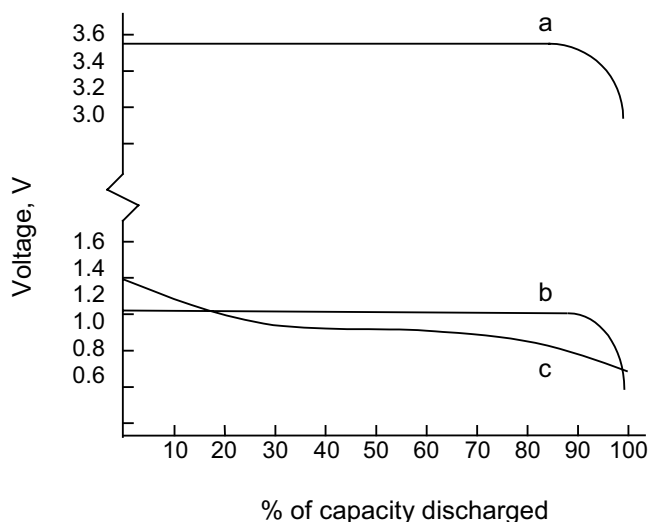
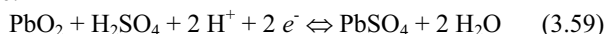


Figure 3.21. Typical discharge plots for AA primary batteries (a) Li/SOCl₂ (b) Zn-Air (c) Zn-MnO₂. Reproduced from Reference 36, Copyright (2002), with permission of The McGraw-Hill Companies.

Positive Electrode:



Negative Electrode:



From the above equations, it can be seen that during discharge, lead sulfate is the main product for both the cathodic and anodic reactants. Sulfuric acid serves as a reactant as well as an electrolyte in this battery. Water is also a product. Thus, during discharge, there is a dilution of the sulfuric acid electrolyte. The active materials formed during charging are lead, lead dioxide, and sulfuric acid. During charging, there is an increase in the electrolyte concentration. Hence, we can use the change in concentration of the electrolyte as a measure of the state of charge. Because of the highly positive reversible electrode potential of the positive electrode ($V_r = 1.65\text{V}$) and of the high negative reversible electrode potential of the negative electrode ($V_r = -0.35\text{V}$), and those being above and below the reversible potentials for oxygen evolution and hydrogen evolution, respectively, these gases are evolved during charging of the lead acid battery. However, these amounts are relatively small because PbO_2 and Pb have very low electrocatalytic activities for these electrochemical reactions. The hydrogen evolution reaction is the main contributor to the self-discharge of the lead acid battery.

The most common cell design has a plate construction. Plate constructions are of two types: grid plate or pasted plate. A grid network contains the active material in pellet form. Lead oxide (PbO) is the starting material for the preparation of the plates. The active materials (Pb and PbO_2) in the plates are produced electrochemically. The plates are then assembled in the cell. Individual cells are connected in series to attain the desired battery voltages. Several types of materials have been used for the separators between the anode and cathode—e.g., cellulose, microglass, sintered polyvinyl chloride, synthetic wood pulp. Microporous separators are preferred for starter batteries. The basic functions of the separator material are to retain the electrolyte in their microporous structure and to prevent electronic contact between the positive and negative electrodes.

Auxiliaries include vent caps to exhaust acid fumes and valve plugs to release gas pressure. Small amounts of palladium are used to recombine hydrogen and oxygen produced during charging. Automatic refilling systems are used in traction batteries.

- (c) *Applications and economics.* The most common application worldwide of lead acid batteries is as a starter battery for transportation vehicles. These are commonly referred to as SLI batteries (starter-lighter-ignition). There has been great interest in using lead acid batteries for traction. In fact, the electric automobiles in the beginning of the 20th century used lead acid

batteries as the power source. But due to the rapid progress made in internal combustion engine and diesel powered engine vehicles, the interest was greatly diminished. There was a revival in the development of lead-acid battery technology for electric vehicles since the late 1980's to the mid 1990's but due to the low range of those vehicles (less than 150 km) and long time (5 to 7 h) needed for charging, the interest for developing such vehicles greatly decreased. However, as seen from the Ragone plot (Figure 3.22), even though lead acid batteries have a low energy density, they could attain high power densities. Thus, these batteries are still being considered as the second power source with the primary internal combustion engine (ICE) or diesel engine power plants for hybrid electric vehicles. But here too, because of the comparably higher energy densities attained with Ni/MH_x and lithium ion batteries, the latter types of batteries are the desired batteries for hybrid electric vehicles (HEVs) at the present time. At a considerably higher energy storage level, lead acid batteries are used for standby/emergency power by telephone companies, hospitals and electric power generation companies.

As indicated in Table 3.20, lead acid batteries have the predominant share of the battery market. The cost of the battery is variable, depending on its design and capacity. The SLI battery costs about \$100/kWh, while

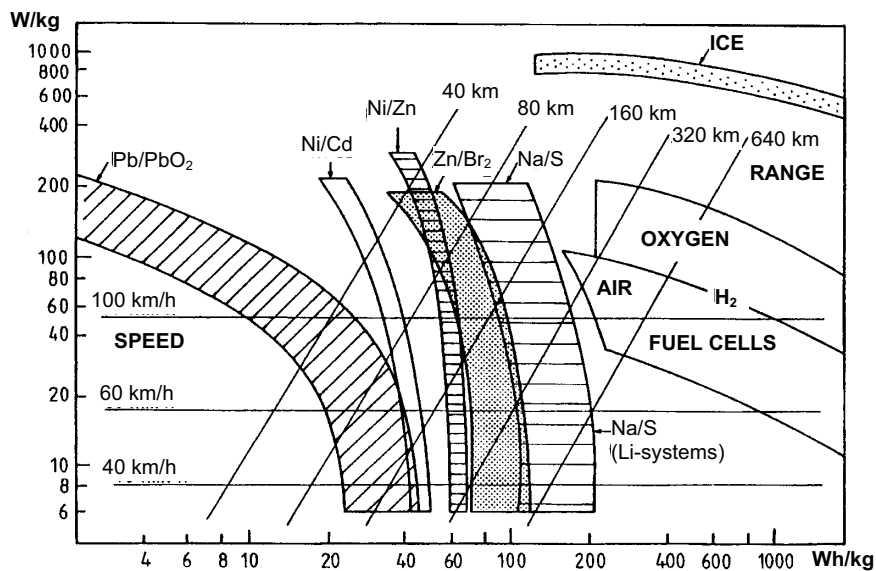


Figure 3.22. Ragone plots for some batteries and fuel cells, an electrochemical capacitor and a PEMFC. Modified from Cited Reference 42.

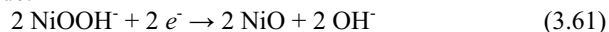
batteries with relatively low capacity may have a cost five to ten times higher. One attractive feature of the lead acid battery is that practically 100% of its lead content can be recycled. This is a significant feature, considering the fact that lead is a toxic element and thus an environmental pollutant.

- (d) *Benefits to or from fuel-cell technology.* The Ragone plot (Figure 3.22) clearly show that lead acid batteries have a low specific energy density but can attain a high power density while it is the reverse in the case of fuel cells. Thus, in order for the fuel-cell powered vehicles to be competitive with IC or diesel engine powered vehicles, it is necessary for the former to have a hybrid power source. The lead acid battery could serve this function quite well. It still faces stiff competition from Ni/MH_x and lithium ion batteries for this function. But from an economic point of view, the lead acid battery is the more favored choice (see Table 3.20). Another relevance to fuel cells is that fuel cell electrocatalysts could be used for the recombination of hydrogen and oxygen evolved during overcharging of lead acid batteries.

3.7.3.2. Nickel/Hydrogen

- (a) *Background and applications.* The Ni/H₂ battery contains the best of both worlds in respect to the positive and negative electrodes—one of the best battery electrodes, i.e., the nickel oxide electrode, and the ideal hydrogen electrode, as in a hydrogen oxygen fuel cell. Both these electrodes have very low activation overpotentials, in the charging and discharging modes. Furthermore, the cycle life of the battery can be as high as tens of thousands of cycles. It is for this reason that it is mainly used in satellites in the low earth (LEO) and geosynchronous earth orbits (GEO).
- (b) *Principles of technology.* The overall reaction in a Ni/H₂ battery, its standard thermodynamic reversible potential and its specific energy and energy density are as stated in Table 3.21. The half cell reactions are as follows:

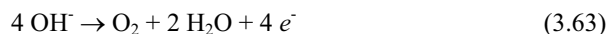
Positive Electrode:



Negative Electrode:



During overcharge, oxygen is evolved at the nickel oxide electrode;



The oxygen, however, is reduced chemically and electrochemically at the positive electrode as:



and



Even though some of the hydrogen evolved during charging has free access to the nickel oxide electrode, it does not cause any problem because of the slow kinetics of electrooxidation of hydrogen on the nickel oxide electrode. For this reaction, it is necessary to have metallic nickel for the initial step of dissociative adsorption of hydrogen. The electrolyte in the cell is 8 M KOH. The cells operate in the temperature range of about 10 to 50 °C. The hydrogen evolved during charge is pressurized

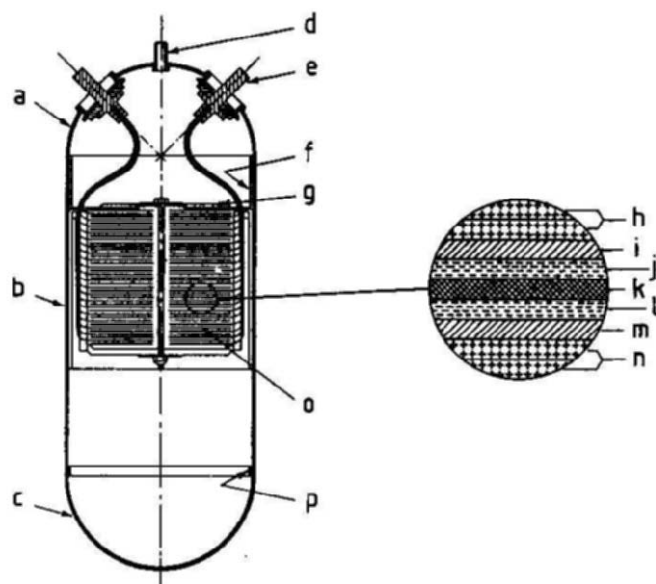


Figure 3.23. Construction of a nickel oxide-hydrogen cell, showing details of the cell construction. a) Container top hemisphere; b) Container cylindrical section; c) Container bottom hemisphere; d) Filling tube; e) Terminal; f) Welding ring; g) Pressure plate; h) Positive electrode; i) Separator; j) Negative electrode; k) Gas diffusion screen; l) Negative electrode; m) Separator; n) Positive electrode; o) Electrode stack; p) Welding ring. Reproduced from Reference 38, Copyright (1985), with permission from Wiley-VCH.

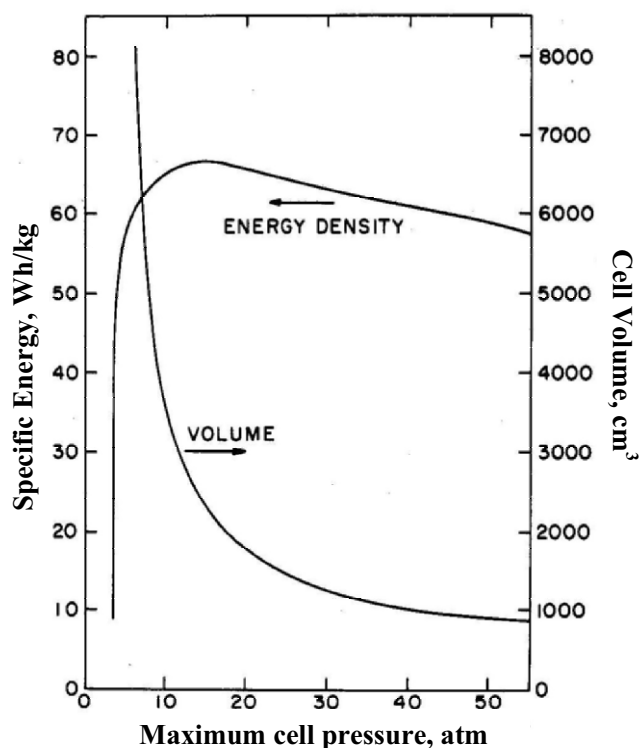


Figure 3.24. Dependence of specific energy and cell volume on maximum pressure for a Ni/H₂ battery. Reprinted from Reference 39.

(~ 50 atm). The cells operate in the pressure range 3 to 50 atm. The battery may be in a common pressure vessel or it may consist of cells in individual pressure vessels. A schematic of a battery in a common pressure vessel is illustrated in Figure 3.23. The dependence of specific energy and cell volume on maximum pressure is shown in Figure 3.24. It is assumed in this figure that the minimum pressure during operation of the battery is 3–4 atm. For the satellite application, the Ni/H₂ battery is charged with photovoltaic systems during daylight and the battery generates electric power during the dark period. Typical discharge plots for the Ni/H₂ battery are as illustrated in Figure 3.25. These plots clearly demonstrate that it is an ideal battery with minimal overpotential losses.

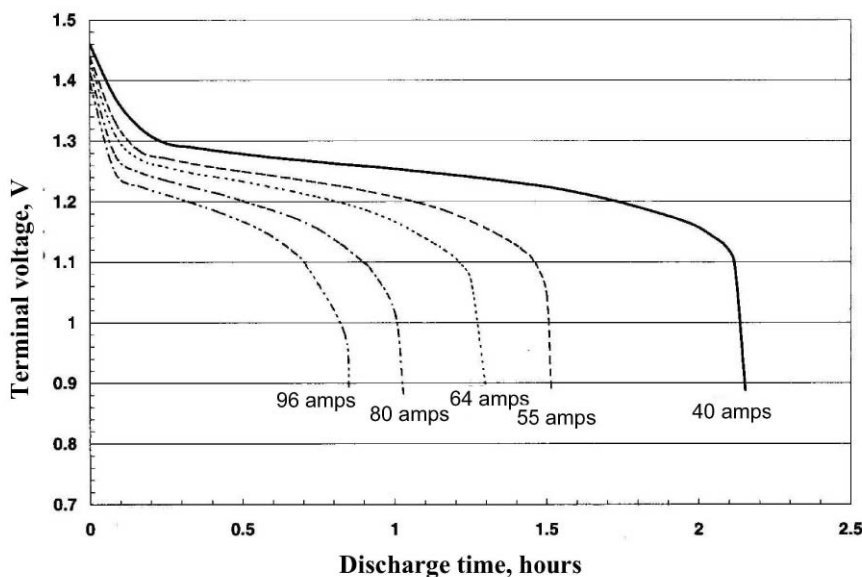


Figure 3.25. Discharge plots for a 90 Ah Hubble Space Telescope Ni/H₂ battery at different rates. Reproduced from Reference 36, Copyright (2002), with permission of The McGraw-Hill Companies.

To reduce the pressure in a Ni/H₂ battery, there have been several efforts to store the hydrogen as a metal hydride (e.g., LaNi₅H_x) or use hydride electrodes. In the latter case, the battery will be of the nickel/metal hydride type (see Section 3.7.3.4).

- (c) *Applications and economics.* The main application of this battery is for satellite power. The capacity of the battery is in the range 90 Ah. The battery voltage is about 1.2–1.3 V during discharge. For the LEO application, charge/discharge cycles are of equal duration per day, while for the GEO cycles, the charging time is about 20 h and discharge time is 1–2 h. The Ni/H₂ battery uses conventional nickel oxide electrodes as in Ni/Cd and Ni/MH_x batteries (see next two Sections) for the positive electrode and highly Pt loaded fuel cell electrodes (more than 4 mg/cm²) for the negative electrode. The latter makes the battery cost quite high (\$1000/kWh). If the cost of the battery can be significantly reduced, it can be considered for terrestrial application, e.g., vehicle propulsion, standby/energy power. One drawback of the battery is that the self-discharge rate is about 10%/d at 20 °C.

- (d) *Expected benefits to or from fuel-cell technology.* The Ni/H₂ battery technology development has obtained maximum benefits from fuel cell technology in respect to the production of high performance hydrogen electrodes that perform most efficiently in the charging and discharging modes.

3.7.3.3. Nickel/Cadmium

- (a) *Background.* Ni/Cd batteries were invented by Jagner long after the lead acid batteries were developed. It was originally proposed that the Ni/Cd battery could be a power source for electric vehicles. This battery uses a nickel oxide positive electrode, as in all other alkaline nickel batteries, and a negative cadmium electrode. The Ni/Cd battery is better than the Ni/Zn or Ni/Fe batteries, which were discovered in the same time period. The reason for this is because the Cd/Cd(OH)₂ system is quite stable (Cd(OH)₂ is formed during discharge), while the products of zinc or iron electrooxidation can dissolve to a significant extent in the potassium hydroxide electrolyte. The latter problem causes morphological changes during charging of the battery. Other advantages of the Ni/Cd battery are its high rate capability, long cycle life, and good low temperature behavior.
- (b) *Principles of technology.* The overall reaction in a Ni/Cd battery, its reversible potential, and its attained energy density are as stated in Table 3.21. The half-cell reactions, during charging and discharging of the nickel electrode, are the same as in the Ni/H₂ battery (Eq. 3.61). The half-cell reaction at the negative Cd electrode is $\text{Cd} + 2 \text{OH}^- \rightleftharpoons \text{Cd(OH)}_2 + 2 e^-$.

The thermodynamic reversible potential for this electrode is -0.809 V. Taking into account that the standard reversible potential for the positive nickel oxide electrode is 0.490 V, the standard reversible potential for the cell is 1.229 V. The theoretical specific energy of the cell is about 200 Wh/kg, based on the mass of the active materials, but as seen from Table 3.21, the maximum attained value is less by a factor of four to five, due to some irreversibilities and ohmic losses. The charge/discharge cycles are around 70% of the theoretical capacities.

In respect to electrode structures and materials, a porous sintered nickel plaque is used as the substrate for the deposition of the active materials (positive and negative electrodes). It has a porosity of 80% and contains a nickel screen as a current collector for the positive electrode; the active material is then deposited by using a vacuum impregnation method. The impregnation is carried out using 4 M Ni(NO₃)₂. An alternative approach is via the electrochemical impregnation of Ni(OH)₂ by cathodizing the plaque in a nickel nitrate solution. The cathode current reduces the nitrate ion to ammonia. The simultaneous increase in the pH precipitates Ni(OH)₂ in the pores of the plaque. The cadmium electrodes

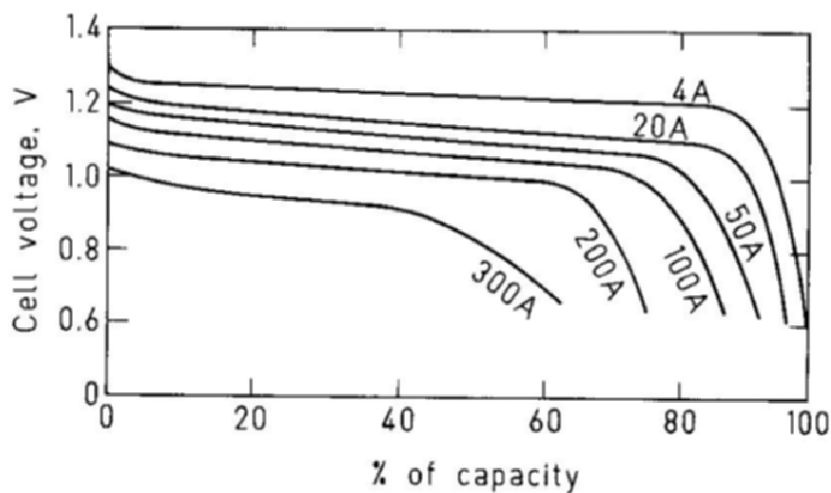


Figure 3.26. Typical discharge behavior at different rates for Ni/Cd batteries. Reproduced from Reference 38, Copyright (1985), with permission from Wiley-VCH.

are produced in a similar manner. Another approach for the manufacture of the cadmium electrodes is by binding cadmium oxide with polytetrafluoroethylene. This layer is then rolled onto a nickel current collector.

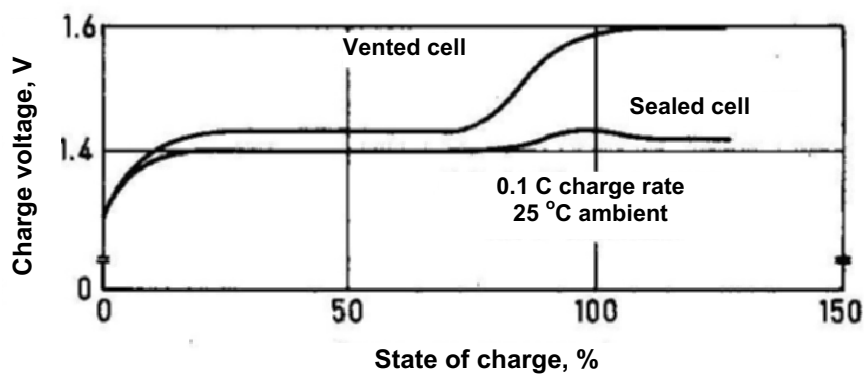


Figure 3.27. Charging behavior of vented and sealed Ni/Cd batteries. Reproduced from Reference 38, Copyright (1985), with permission from Wiley-VCH.

There are two types of cell design: vented cells and sealed cells. The former are flat-plate prismatic cells and the latter have a cylindrical configuration. In the vented cells, microporous propylene or radiation-grafted polyethylene membranes are used as separators. The electrolyte is 8 M KOH with small amounts of LiOH. The latter enhances the capacity of the nickel electrode. The sealed cells have a Swiss-Roll type construction. The separator material is woven nylon in non-woven polyamide felt. The electrolyte is embedded in the separator. Gas-venting is provided to inhibit pressure build up during charging.

The batteries of choice are the Ni/Cd batteries for high rates of charge and discharge. Typical discharge behavior at different rates is illustrated in Figure 3.26. There is some significant drop in capacity only above the 5 °C rate. The charging behaviors for a vented and a sealed cell are shown in Figure 3.27. Up to about a 75 % state of charge, the charge voltage is constant, while there is a rise in it above this voltage. This is because of some hydrogen and oxygen evolution reactions that have higher activation overpotentials.

The charge-retention characteristic of the vented Ni/Cd battery is excellent, over 70% retention after six months of charging. The self-discharge rate in sealed Ni/Cd batteries is somewhat higher. Likewise, the cycle life of this battery is very high. It is more than a few thousand cycles for a charge exchange of 70%. For aerospace applications at lower rates of charge and discharge, the cycle life range is in the tens of thousands.

- (c) *Applications and economics.* For a considerable length of time, Ni/Cd batteries have had the second highest share of the secondary battery market. The main applications have been for standby or emergency power, aircraft auxiliary power, power sources for portable equipment (calculators, tools, laptop computers, video cameras, toys, etc.). Until recently, it also was used extensively in satellites, but due to the superior behavior of Ni/H₂ batteries, Ni/Cd batteries are being gradually displaced. Ni/Cd batteries were also researched on to power electric vehicles. For most of the above-mentioned terrestrial applications, the Ni/Cd batteries have been replaced by Ni/MH_x batteries, which have somewhat similar performance characteristics because of the toxicity problems of cadmium. There are environmental legislations in several countries, particularly Japan, to terminate the production of Ni/Cd batteries. Thus, the costs of Ni/Cd batteries have significantly decreased to about \$ 400/kWh.
- (d) *Benefits to or from fuel-cell technology.* There are no clear benefits to or from fuel cell technology in the case of Ni/Cd batteries. However, one application which has been proposed for a long time, was to use the Ni/Cd battery as the hybrid power source with fuel cells for electric vehicles. The main reasons are because of its higher specific energy, specific power, and longer cycle life than the lead acid battery.

3.7.3.4. Nickel/Metal Hydride

- (a) *Background and rationale.* Since the early 1960s, storing hydrogen in metals and alloys has attracted much attention. The pioneering work was carried out by researchers at Brookhaven National Laboratory in Upton, NY and the Philips Research Laboratory in Eindhoven, Netherlands. In principle, there are several metals and alloys that can adsorb and desorb hydrogen to the extent of one atom of hydrogen for each atom of the metal. The extent of hydrogen storage is about 1% for transition metals like iron and about 6% for lighter metals such as magnesium. Alloys have been found to be superior to the pure metals for fast adsorption/desorption kinetics. Conventionally, two types of alloys AB_5 (e.g., $LaNi_5$) and AB_2 (e.g., VTi_2) have been used for the metal-hydride electrodes. However, for hydrogen-storage applications, the alloy formulations (atomic %) are much more complex, as shown below:

- $AB_5 - La_{5.7}Ce_{8.0}Pr_{0.8}Nd_{2.3}Ni_{59.2}Co_{12.2}Al_{5.2}$
- $AB_2 - V_{18}Ti_{15}Zr_{18}Ni_{29}Cr_5Co_7Mn_8$

The benefits for incorporating more elements than only two in each alloy are:

- better kinetics for adsorption/desorption of hydrogen,
- inhibition of passivation of active components on the surface, and
- facilitation of dissociative adsorption of hydrogen

to name a few.

From the time period that metal hydrides were researched on for hydrogen storage, there has been great interest in these alloys for nickel/metal hydride batteries. The reason is that nickel/metal hydride batteries exhibit performance characteristics practically identical to nickel/cadmium batteries. The advantages of the former over the latter are:

- nearly the same reversible potential for the cell (about 1.35V),
- similar charge-discharge characteristics,
- higher energy density and specific energy, and
- most importantly, the toxic element cadmium is replaced by practically harmless metals.

Since the early 1990s, Japanese companies (Matsushita, SONY, Sanyo) have been developing and commercializing Ni/MH_x batteries. But more recently, the technology and commercialization have spread to several other countries—e.g., Korea, Taiwan, and China. A bulk of the batteries is used for portable applications—laptop computers, cell phones, and other consumer electronics applications. There are ongoing efforts to use higher capacity batteries for hybrid electric vehicle applications.

- (b) *Principles of technology.* The active material in the positive electrode (NiOOH) is the same as in the Ni/H₂ and Ni/Cd batteries, as discussed in the two preceding Sections. The active material in the negative electrode is the alloy hydride. The half cell reaction is:



where M represents the alloy. In practically all the batteries, AB₅ alloys are being used, even though the AB₂ alloys have higher specific energies and energy densities. The advantages of the former are:

- higher charge/discharge rates and
- better performances at higher and lower temperatures than 25 °C.

A desired formulation for the multicomponent AB₅ alloy has been quoted above. However, in the large-scale manufacture of the batteries, a naturally occurring ore, misch metal, which has most of the desired constituent alloys, is used with some modification to enhance kinetics and improve stability and the cycle life.

As to the designs of the batteries, they are of the cylindrical (Figure 3.17), button, and prismatic cell types (Figure 3.18). The positive electrodes have the same structure and composition as in the Ni/H₂ and Ni/Cd batteries. The negative electrode has a highly porous structure, with a perforated nickel foil or grid, containing the plastic bounded hydrogen storage alloy. A typical multi-cell battery (9 V) is illustrated in Figure 3.28.

The discharge behavior of a Ni/MH battery is shown in Figure 3.29. There is some decrease in performance at temperatures below about 10 °C and above 45 °C. The region in between is the ideal one for battery operation. The cycle life of the battery has improved over the years. The charge retention rate of the battery is quite satisfactory; it is better at close to room temperatures.

- (c) *Applications and economics.* For the portable applications, the types are practically the same as in the primary Zn/MnO₂ and secondary Ni/Cd batteries (e.g., A, AA, AAA, C, D, 9 V). One significant advantage of this battery is that its sealed cell uses an oxygen recombination mechanism to prevent pressure build up during cell charging and overcharging. For this purpose, the negative electrode has a higher effective capacity than the rated one. Thus, the oxygen, evolved during overcharge at the positive electrode, diffuses through the separator to the positive electrode and combines with the MH to form water, while the hydride electrode is never overcharged because of the higher capacity. The larger batteries are similar in design and construction to the Ni/Cd batteries. These are the

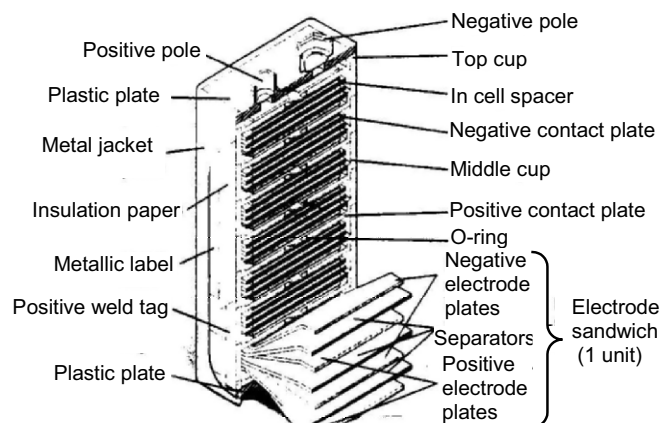


Figure 3.28. Typical design of a multicell Ni/MH battery. Reproduced from Reference 36, Copyright (2002), with permission of The McGraw-Hill Companies.

hybrid power sources, with the IC engines in the Toyota Prius and Honda Civic vehicles. For the portable electronics application, the cost of the batteries is comparable to that for the Ni/Cd batteries; for the hybrid electric vehicle operation, the projected cost is \$300–400/kWh.

- (d) *Benefits to or from fuel-cell technology.* The optimization of the composition of the MH electrode has benefited from the development of fuel cell electrocatalysts for the hydrogen electrode, particularly in alkaline medium, as for instance, incorporating nickel or cobalt. These elements enhance the activities for dissociative adsorption of hydrogen and/or inhibit formation of passive films or corrosion of the alloys. It must be noted that the standard reversible potential for the Ni/MH_x battery is the same as for the hydrogen electrode in fuel cells. It is for this reason that there has been some developmental work of metal hydride/air batteries. The hydrogen storage and the hydrogen electrode charging/discharging characteristics are carried out in the sealed secondary battery.

3.7.3.5. Lithium–Ion

- (a) *Background and rationale.* At the present time and for the foreseeable future, the rechargeable lithium-ion batteries will be in the forefront for consumer electronic (cell phones, laptop computers) and military electronic (radios, mine detectors, thermal weapon sites) applications. Potential applications are for aircraft, spacecraft, and for hybrid electric vehicles (IC or diesel/battery). The attractive features of this battery are:

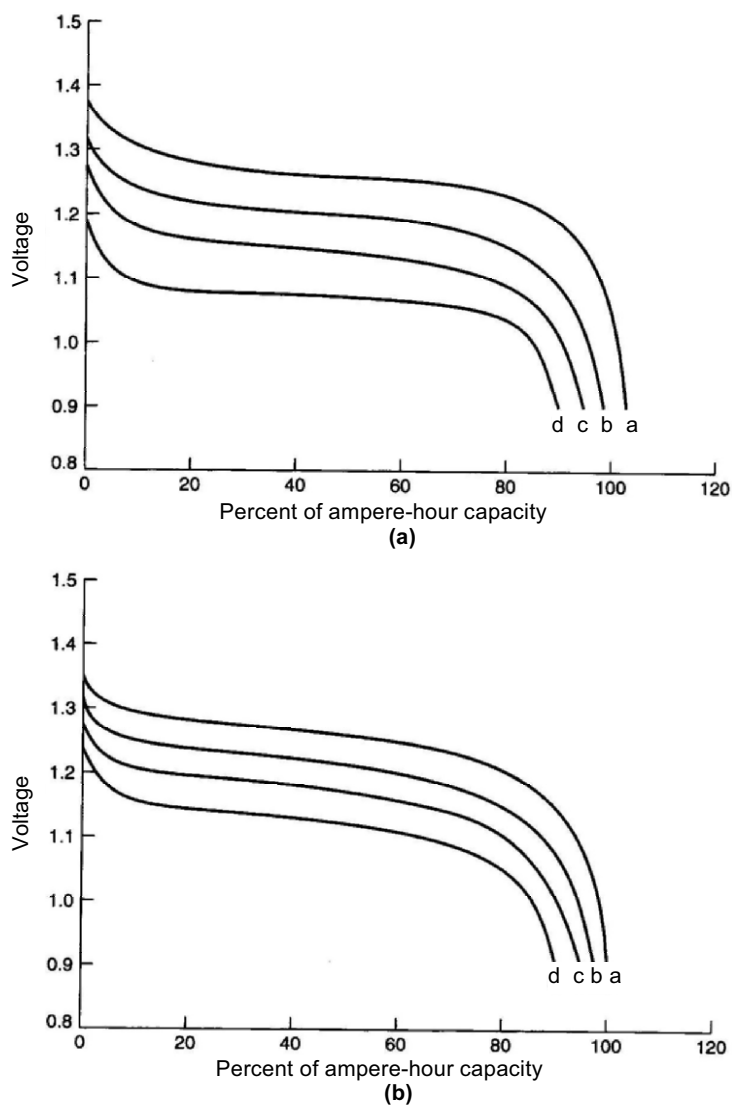


Figure 3.29. Charge/discharge behavior of a nickel metal hydride battery at (a) 25 °C and (b) 45 °C. The symbols a, b, c, and d represent discharge rates of C/5, C, 2C, and 3C, respectively, with C Being defined as the discharge current in amps divided by the rated capacity of the battery in ampere-hour. Reproduced from Reference 36, Copyright (2002), with permission of The McGraw-Hill Companies.

- high energy density,
- high power density, and
- low self-discharge rate.

A significant advantage of this battery is that its range of operating potential is from about 2.5 to 4.2 V; this is about three times higher than that for the competing secondary batteries, such as nickel/hydrogen, nickel/cadmium, and nickel/metal hydride. Thus, to operate in this potential range for any application, only one-third the number of Li-ion cells is required in a stack, as compared with that for the other above-mentioned batteries. It is noteworthy to mention that the fundamental research studies on the electrodes and electrolytes have been carried out, over the last 20 years, at universities and national and industrial laboratories in the USA, Canada, and France; soon after, this was followed by intensive R&D efforts in Japanese laboratories. However, the mass production of these batteries (over 90%) for the consumer and military electronic applications is by Japanese companies (e.g., SONY, Matsushita, Sanyo, to name a few).

- (b) *Principles of technology.* The lithium-ion battery has a unique characteristic: it operates by transport mechanism of a lithium ion, from the positive electrode to the negative electrode during charging and vice versa during discharging. For both electrodes, intercalation materials are used. The present batteries mostly use coke for the negative electrode material and lithium cobalt oxide (LiCoO_2) for the positive electrode materials. Alternatives are graphite for the former and lithium manganate (LiMn_2O_4), lithium-nickel-cobalt oxide ($\text{LiNi}_{1-x}\text{Co}_x\text{O}_4$) for the latter. Since lithium is a highly electropositive material, an aqueous electrolyte medium cannot be used (due to the rapid rate of hydrogen evolution). Thus, one has to employ organic solvents or ceramic electrolytes. The former are considerably better and are used in practically all the commercial batteries. The organic solvents include ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), acetonitrile (AN), tetrahydrofuran (THF), and several others.

In order to have ionic conduction of lithium ions in the electrolyte, inorganic or organic lithium salts are dissolved in the organic solvent. The most widely used material is lithium hexafluorophosphate (LiPF_6). Several other materials have been evaluated and some are already in use in lithium-ion batteries, e.g., lithium tetrafluoroborate (LiBF_4), lithium perchlorate (LiClO_4), lithium hexafluoroarsenate (LiAsF_6), and lithium triflate (LiSO_3F). Safety considerations have to be taken into account in the selection of both the salt and the solvent. The electrolyte can be in liquid or gel form (the latter types of batteries are commonly referred to as lithium polymer batteries). Lithium-ion batteries with the liquid electrolyte have higher ionic conductivities (10^{-3} to 10^{-2} S/cm); the

conductivities of the lithium polymer batteries are at least an order of magnitude lower. For the lithium-ion cells with a liquid electrolyte, a separator material is required to prevent contact between the positive and negative electrodes; microporous films (10 to 30 μm) of polyolefin materials (polyethylene, polypropylene, or laminates of the two) are used for this purpose. A commercial material used in some batteries is Celgard.

The most common designs of the cell are of the spiral-wound cylindrical and flat-plate prismatic types. This is for capacities ranging from 0.1 to 160 Ah. The batteries are prepared in the discharged state—for this purpose the positive electrode material is the lithium metal oxide and the negative electrode material is coke. But more recently, the manufacturers are increasingly using graphitic materials for the latter because of their higher specific capacity, cycle life, and rate capability. Both of these materials in powder form are bonded on to a metallic foil or a screen (aluminum for the positive electrode and copper for the negative electrode). The cell is then assembled with the electrolyte and the cell is charged and lithium ions are transferred from the positive to the negative electrode. Care must be taken during the first charging not to exceed about 4.2 V. Above this voltage, side reactions such as oxidation of the solvent may occur. During charging/discharging, the potential range has to be regulated between 2.5 and 4.2 V to avoid reaching the maximum and minimum voltage.

The reactions, which take place at the electrode/electrolyte interfaces and in the single cell, can be represented by the equation:

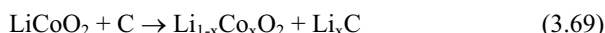
Positive electrode:



Negative electrode:



Overall:



During charging all the lithium from the LiCoO_2 is not released. Customarily, x reaches a maximum value of about 0.8 (a capacity equivalent to about 80% of the theoretical capacity is attained). It has been demonstrated that the ratio of lithium to carbon atoms has a maximum value of 1:6. Thus, the theoretical capacity of the lithium electrode is 372 mA h/g, which is about 10% of that if pure Li were used for the negative electrode. Pure lithium cannot be used as the positive electrode material because the interaction of the metal with the solvents can lead to explosions.

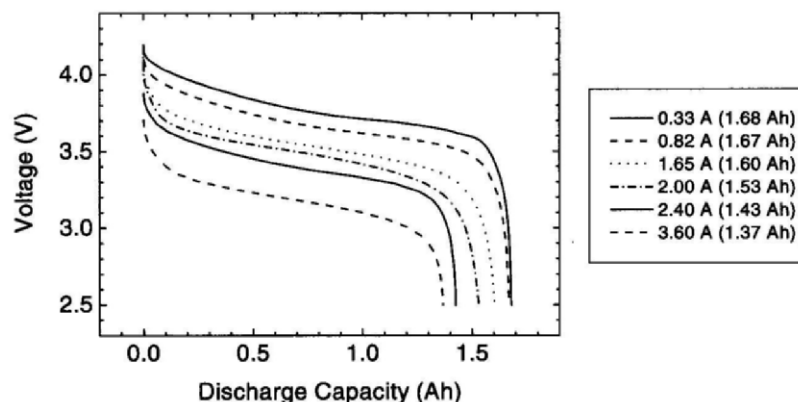
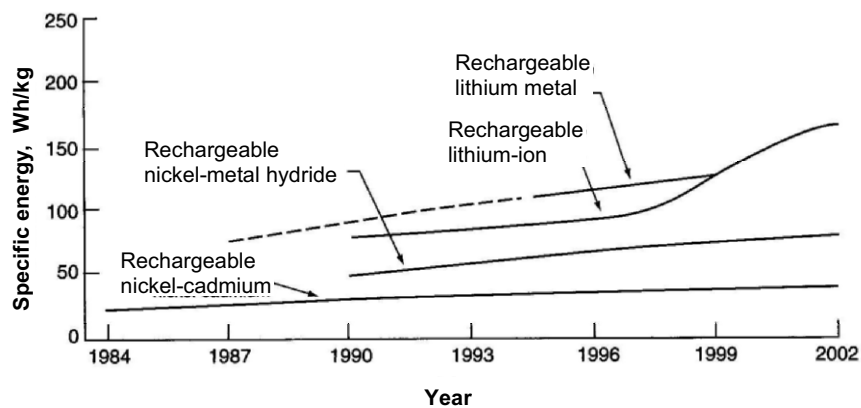


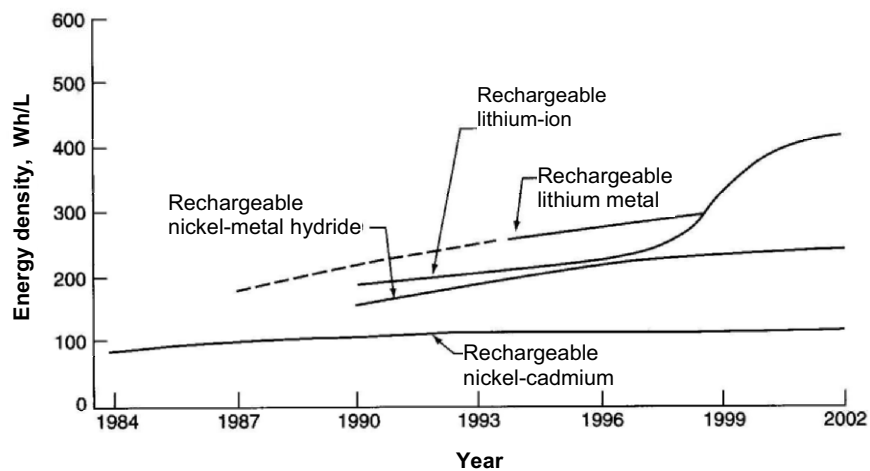
Figure 3.30. Typical discharge behavior of a Li-ion battery. Reproduced from Reference 36, Copyright (2002), with permission of The McGraw-Hill Companies.

The highly advantageous performance characteristic of a lithium-ion battery is reflected in its charge/discharge behavior (Figure 3.30); it has a far superior behavior, in comparison with that of nickel/hydrogen, nickel/cadmium, and nickel metal hydride batteries (see the three preceding Sections). The discharge potentials are relatively flat as a function of discharge capacity and are about 3 times higher for the lithium-ion batteries, as compared with those for the nickel-batteries. The lithium-ion batteries can also be operated at high charging/discharging rates (up to about 3–5 °C). The cycle life of the lithium battery has greatly improved during the last 5 years, over 1000 cycles. This is still a factor of 10 less than that attained for the aforementioned alkaline nickel batteries. However, for the portable consumer and military applications, the attained cycle life is adequate. For the transportation, space, and satellite applications, a longer cycle life is essential.

- (c) *Applications and economics.* The demand for the lithium-ion batteries for the portable consumer/military electronic products has been growing exponentially since the mid 1990's. The number of units of lithium-ion batteries will be about 1.3 billion in the year 2007.⁷ This amount is about twice that sold in the year 2000. Other interesting data are the enhancements made in the specific energies and energy densities of the battery—e.g., see Figure 3.31 for a much marketed lithium-ion cylindrical battery, since the early 1990s until the present time, in comparison with rechargeable Ni/Cd and Ni/MH batteries.
- (d) *Benefits to or from fuel-cell program.* The fuel cell technology is markedly different from the lithium-ion technology and thus, the reader



(a)



(b)

Figure 3.31. Enhancement in performance of portable rechargeable batteries (a) specific energy (b) energy. Reproduced from Reference 36, Copyright (2002), with permission from The McGraw-Hill Companies.

may not be able to visualize any technical benefits. However, the lithium-ion battery will be a strong contender for powering hybrid electric vehicles. In the long term, it may be more advantageous than the nickel-metal hydride batteries because of the higher-performance characteristics of the lithium-ion battery, achieved and projected. In the long term, the fuel cell will be the primary hybrid power source and will replace the IC or diesel engine.

3.7.4. Reserve Batteries

3.7.4.1. Background and Rationale. Reserve batteries have been developed and utilized for special applications. These applications require one or more of the following specifications:

- long shelf life,
- low self-discharge rate,
- high power density and specific power for short times, and
- high energy density and specific energy.

The applications include their uses in:

- torpedoes, missiles, and other weapons,
- lifeboat emergency equipment in commercial airlines,
- radios,
- sono buoys, and
- balloon transport equipment for high altitude and low ambient temperature operation.

There are four types of reserve batteries:

- water activated (by fresh or sea water),
- electrolyte activated by its injection,
- gas activated (e.g., air), and
- heat-activated (e.g., a solid salt electrolyte is connected to the molten state to become ionically conducting).

Water or seawater activated batteries are the most common types of reserve batteries. The active components of the reserve batteries are:

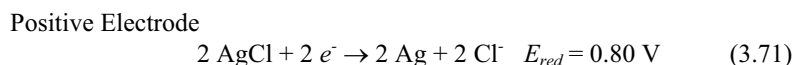
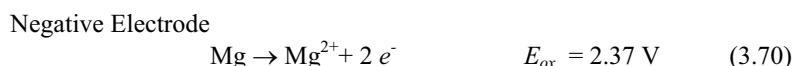
- corrodible metals like lithium, magnesium, aluminum, or zinc for the negative electrode, and
- silver chloride, cuprous chloride, lead chloride, manganese dioxide, or cuprous iodide for cathode materials. In some cases, air is the cathodic reactant.

Because of space limitations in this book, we shall present a short summary of magnesium-seawater activated batteries using silver chloride as the cathodic

reactant. The reader is referred to *the Handbook of Batteries* edited by Linden and Reddy for more detailed descriptions.

3.7.4.2. Mg-Seawater Activated Batteries

- (a) *Principles of technology.* These batteries use magnesium or a magnesium alloy for the negative electrode and silver chloride, cuprous chloride, lead chloride, cuprous iodide, or magnesium dioxide for the positive electrode. Batteries have also been developed with air as the cathodic reactant. In the case of the Mg/AgCl battery, the half cell reactions are:



The overall reaction is represented by the addition of the two above-mentioned half-cell reactions, as seen in Table 3.20. Batteries are produced with the anode, cathode, and separator in the dry state. The battery is activated by introduction of the electrolyte. There are several types of these water activated batteries: two of these are (i) immersion batteries which are activated by immersion in water or seawater, and (ii) forced-flow batteries, used for torpedoes, in which sea water is forced through the battery as the torpedo is driven through the water. A multi-cell stack in the battery can produce about 500 kW of power in about 15 min. Attained values of specific energy and energy density are 130 Wh/kg and 200 Wh/l.

- (b) *Applications and economics.* The main application of the Mg/AgCl batteries is in torpedoes. Other types of applications for magnesium-sea water batteries are as described in Section 3.7.4.1. The Mg/AgCl battery is quite expensive because of the high cost of silver and it being non-reversible after use. Thus, instead of AgCl as the cathodic material, Cu_2Cl_2 , Cu_2I_2 , PbCl_2 , and $\text{Cu}_2(\text{CNO})_2$ have been used but the energy densities and specific energies are considerably less in these cases.
- (c) *Benefits to or from fuel-cell technology.* At the present time there are no benefits of the reserve batteries to or from the fuel cell technologies. One exception may be for using better electrodes for oxygen reduction, as developed for alkaline fuel cells, in the batteries which use air as the cathodic reactant.

3.7.5. Thermal Batteries

3.7.5.1. Background and Rationale. This short Section on thermal batteries is included in this Chapter only for the sake of providing the reader with a perspective of all types of batteries. For more details, the reader is referred to an excellent review on thermal batteries by Klasons and Lamb in Chapter 21 of the *Handbook of Batteries*. Thermal batteries are akin to reserve batteries, discussed in the previous Section. The main difference is that during the design and construction of the batteries, the electrolytes are non-conducting, inorganic solids (at room temperature) and interfaced with the anodes and the cathodes. A pyrotechnic material is also incorporated in the material, which when activated, melts the electrolyte and makes it conducting. Immediately after activation and when the battery is connected to a load, the battery discharges for short periods of time. The discharge time depends on the capacity of the anode and cathode and more so falls off with time due to cooling of the battery and solidification of the electrolyte.

Thermal batteries were first developed in Germany, mainly for weapons applications. In order to attain the power levels required, the geometric areas are increased and cell stacks developed. Some examples of military applications are for use in missiles, bombs, and torpedoes. These batteries have also been used for space exploration. Some advantages of these batteries are:

- long shelf life (~ 25 years) without degradation in performance and no self-discharge,
- start-up time in milliseconds,
- peak power of about 10 W/cm²,
- high reliability, and
- wide range of operating temperature.

The disadvantages of these batteries are:

- short periods of power generation (~ 10 min),
- low to moderate specific energies and energy densities,
- surface temperatures reach over 200 °C,
- power output decreases with time of discharge, and
- use for only one time, like a primary battery.

3.7.5.2. Principles of Technology and Performance Characteristics. The anode materials are the highly electropositive alkaline or alkaline metals or their alloys (e.g., Li, Si, Mg, Cu) and the cathode materials are strong oxidants (e.g., K₂Cr₂O₇, CaCrO₄, V₂O₅, FeS₂). The electrolytes are alkali halides (e.g., LiCl-KCl, LiBr-KBr, LiBr, KBr-LiF). The conducting species in the electrolyte is the lithium ion. There are two types of pyrotechnic heat sources—heat paper and heat pellets. The heat paper typically contains zirconium and barium chromate powders, impregnated in an inorganic fiber matrix. Heat pellets typically contain a mixture of iron powder and potassium perchlorate. When the power from the battery is

required, bridge wires and a heat-sensitive pyrotechnic material are used to ignite the pyrotechnic material, which in turn rapidly melts the electrolyte. The discharge voltage range for the batteries using the anode and cathode materials mentioned above is 1.6 to 3.3.

The most widely used thermal battery is the Li/FeS₂ battery, with LiCl-KCl or LiCl-LiBr-LiF as the electrolyte. The overall reaction is:



Cell designs are of three types: cup cells, open cells, and palletized cells. A cup cell contains an anode having the active anode material on both sides of a current collector. On the external sides of the anode material is positioned a glass tape pad impregnated with the eutectic electrolyte. On the external sides of the electrolyte pad are placed the cathode material in an inorganic fiber matrix. Current collectors are placed on the external sides of these fiber matrices. Open cells are similar in design to the cup cells. These types of batteries are used for short time applications and pulse power. Open cells have rapid heat transfer and short activation times. Cell stacks have been designed to meet the power requirements. The cells are connected externally in series. For the above applications, the number of cells is in the range 14 to 80 cells and the discharge voltage is in the range 28 to 140 V. There has been an application for which a stack voltage was 400 V and the number of cells in the stack was 180. For a battery with a volume of 1300 cm³, the performance characteristics were as follows:

- power density: 170 mW/cm²,
- energy density: 85 Wh/l, and
- activated life: 1800 seconds.

In order to advance the Thermal Battery technology, efforts are being made to:

- enhance the specific energy and energy density by using light-weight materials, like aluminum and composites, instead of stainless steel for container materials; and
- use of plasma-spraying techniques for deposition of thin films of FeS₂. Molten nitrates have also been researched as electrolytes with lithium anodes, to enhance cell voltages and reduce operating temperatures by more than 200 °C. Efforts to increase discharge times have been made by using more efficient thermal insulation and lower melting point electrolyte compositions.

3.7.6. Electrochemical Capacitors

3.7.6.1. Introduction. One of the innovations in the field of electrochemical science is the development of electrochemical capacitors, EC, which exhibit a 20–200 times greater capacitance than conventional solid state capacitors. The first electrochemical capacitor was described in 1957 by Becker and Ferry⁴⁰ and it was based on porous carbon. Twelve years later, Sohio developed a carbon-based capacitor in a non-aqueous medium that could be charged to about 3 V. The recognition of the pseudocapacitative behavior during the charging of RuO₂ electrodes, by Trasatti and Buzzanca,⁴¹ triggered a flurry of activity towards developing electrochemical capacitors based on double layer and adsorption pseudocapacitance. Since then there has been a major focus to commercialize these concepts as energy storage and delivery devices, complementary to that by batteries. A thorough discussion of the subject of electrochemical capacitors is available in the authoritative monograph by Conway⁴² and in the proceeding volumes of the annual symposia held by Wolsky and Marincic from 1991 onwards, covering the ongoing progress in this area.⁴³

3.7.6.2. Principles of Technology. The capacitance of a condenser, C , is expressed by the relationship:

$$C = \frac{A\epsilon\epsilon_0}{d} \quad (3.73)$$

where A refers to the area of the plates, d to the distance between them, ϵ to the dielectric constant of the medium, and $\epsilon_0 = 8.84 \times 10^{-12}$ F/m the dielectric permittivity of the free space. The capacitance of the condenser can be increased by increasing the values of the parameters A and ϵ and by decreasing the distance between the plates. The dielectric constant can be increased by forming thin oxide films on the plates made of metals such as Al, Ta, Ti, and Nb. These oxide films, having high dielectric constants, enhance the overall capacitance; these component-devices are called the *electrolytic capacitors*. The energy stored in these capacitors is the free energy, G , which is given by the expression:

$$G = \frac{CV^2}{2} \quad (3.74)$$

where V refers to the voltage applied to the capacitor.

When a metal is immersed in an ionic solution, an electrostatic potential is established at the metal/solution interface (see Chapter 2). This leads to the formation of a double layer as a result of the charge separation occurring on either side of the interface, which is manifested as a displacement current. Note that there is no charge transfer across the interface during this process. The capacitance of the

electrical double layer varies in the range of 16–40 $\mu\text{F}/\text{cm}^2$ depending on the nature of the metal surface and the nature of the solvent and ions present in the system. The reason for high specific capacitance of the electrical double layer at the metal/solution interface is the small distance of separation of charges of 0.3 to 0.5 nm, compared to 10–100 nm in electrolytic capacitors and $> 10^{-3}$ nm with thin mica and polystyrene dielectric film capacitors.

In contrast, when adsorbed intermediates are involved during the course of a Faradaic reaction of the type $\text{O}_{\text{ads}} + ne^- \rightarrow \text{R}_{\text{ads}}$, where O and R refer to the oxidant and reductant respectively, the charge exchanged during the course of the reaction is stored in the form of an adsorbed species. This leads to a pseudocapacitive behavior (see Chapter 2). The capacitance associated with this process is large and is Faradaic and not electrostatic or non-Faradaic in origin. It can be shown from first principles that the generalized impedance, Z , for this reaction is given as:⁴⁴

$$Z(p) = \left(pC_d + \frac{pC_\phi}{pC_\phi R_t} \right)^{-1} \quad (3.75)$$

where p is the Laplace Transform variable, R_t is the charge transfer resistance, C_d is the double layer capacitance, and C_ϕ is the adsorption pseudocapacitance. Hence, the equivalent circuit can be represented as shown in Figure 3.32. The capacitance of this system is expressed by the relationship:

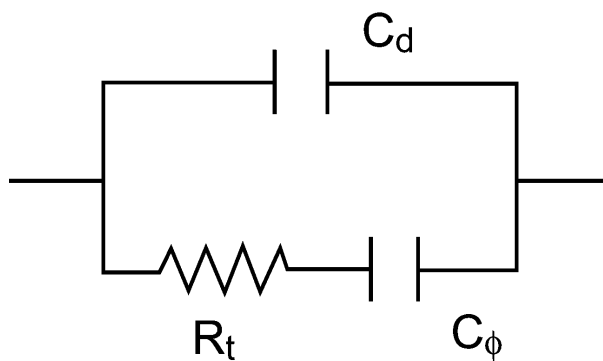


Figure 3.32. Equivalent circuit for a Faradaic reaction exhibiting pseudocapacitance behavior (see text for definition of symbols). Reprinted from Reference 44, Copyright (1996), by permission of The Electrochemical Society, Inc.

$$C = \frac{(C_d + C_\phi)^2 + \omega^2 C_d^2 C_\phi^2 R_t^2}{C_d + C_\phi + \omega^2 C_d^2 C_\phi^2 R_t^2} \quad (3.76)$$

Thus, $C = C_d$ as $\omega \rightarrow \infty$ and $C = C_d + C_\phi$ as $\omega \rightarrow 0$. However, when $R_t = 0$, the overall capacitance will be the sum of the double layer and adsorption pseudocapacitance and is frequency independent. However, if the same reaction is conducted on a porous electrode, the overall capacitance will be frequency dependent and only a fraction of the double layer capacitance is available at short times. As $t \rightarrow \infty$, all the charge associated with the double layer and adsorption pseudocapacity becomes accessible. This is a result of the distributed RC effects in the porous matrix, exhibiting multiple time constants. However, if the electrolyte resistance and the pore length are significantly lowered, then it possible to realize high capacitances at very short times. The maximum pseudocapacitance available with the above reaction is given by the relationship:

$$C_\phi = \frac{n^2 F^2}{RT} \left(\frac{1}{\Gamma_O^0} + \frac{1}{\Gamma_R^0} \right)^{-1} \quad (3.77)$$

where Γ refers to the surface excess of the species in the subscript. C_ϕ can be as large as 8 F/cm² following the above equation with $\Gamma_O^0 = 10^{-8}$ mol/cm² and $n = 2$ with a roughness factor of 100.

Electrochemical capacitors behave like rechargeable batteries in terms of energy storage and delivery, although the mechanisms of charge storage are different from those operating in batteries. The amount of energy stored in the ECs is equal to $CV^2/2$ or $0.5qV$, where q is the amount of charge stored. However, for a battery, the corresponding stored energy is qV , which is twice as much as that for a capacitor charged to the same voltage, since the battery has a thermodynamically constant voltage during charge and discharge except when the state-of-charge approaches 0 or 100%. It may be noted that the energy stored in a capacitor increases with the square of the cell voltage as charge is accumulated.

A wide variety of materials were examined for their capacitive characteristics and a listing of some of them are available in references.⁴²⁻⁴⁴ These can be broadly split into two categories: double-layer capacitors and pseudocapacitance-based capacitors.

- (a) *Double-layer capacitors.* The first EC employed activated carbon as the electrode and it exhibited capacitance values of 2 F/cm² in sulfuric acid solutions. However, carbon was found to suffer from slow oxidation in addition to having a high equivalent series resistance due to poor particle-to-particle contact of the agglomerates and high ionic resistance in the micropores of carbon. Various techniques have been examined to achieve high surface area with low matrix resistivity. These include, use of carbon

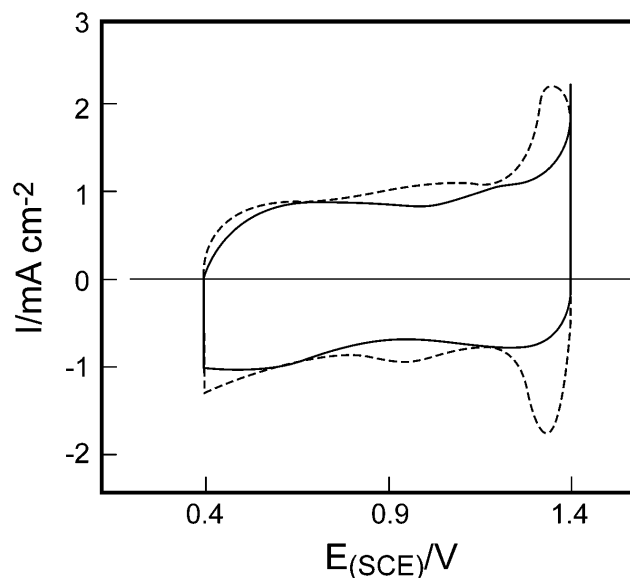
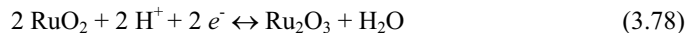


Figure 3.33. Cyclic voltammogram of a ruthenium oxide in acid and alkaline media, exhibiting pseudocapacitance behavior. Reprinted from Reference 45, Copyright (1990) with permission from Elsevier.

foam and paste electrodes, pyrolysis of carbon-based polymers, heat treatment in the presence of additives, addition of Ru, Rh, Pd, Os, Ir, Co, Ni, Mn, Pt, Fe and combinations thereof to carbon.

- (b) *Pseudocapacitance-based capacitors.* Cyclic voltammetric studies showed a broad range of compositions exhibiting adsorption pseudocapacitance. Of all these, RuO_2 -based EC systems showed high specific capacitance due to the C_ϕ arising from the surface reaction:



Capacitances as high as 2.8 F/cm^2 were reported with compositions based on RuO_2 , mixtures of $\text{RuO}_2 + \text{Ta}_2\text{O}_5$, and mixed oxides of Mo, W, Co, and Ni. RuO_2 bonded solid ionomer membranes exhibited 6 to 10 F/g of active material with excellent charge-density delivery in pulse applications. The cyclic voltammogram of a RuO_2 electrode in acidic and alkaline solutions⁴⁵ presented in Figure 3.33 shows significant C_ϕ , which is almost constant over a voltage range of 1.4 V. Some other transition metal oxides behave similarly but only over a small operating voltage

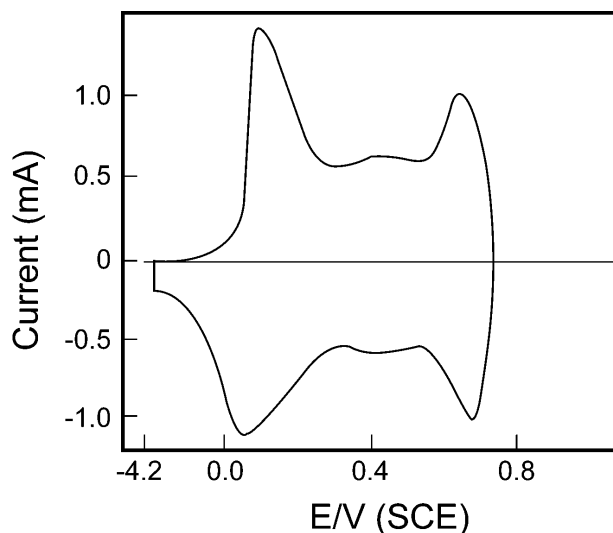


Figure 3.34. Cyclic voltammogram of a polyaniline electrode exhibiting pseudocapacitance behavior.⁴²

range of about 0.6–0.8 V. The reversibility of this system is excellent as it has a cycle life of over several hundred thousand cycles. Electrochemical capacitors based on the RuO_2 electrodes are mainly used in military applications.

Another type of material exhibiting quasi-redox behavior that is highly reversible is the family of conducting polymers such as polyaniline⁴⁶ or derivatives of polythiophene. While they are less expensive than RuO_2 , they are less stable giving only thousands of cycles, between 0.8 V and 3.0 V depending on the material. Figure 3.34 illustrates the cyclic voltammetry of polyaniline, and Figure 3.35 depicts the reversible behavior of RuO_2 and the irreversible nature of Pb/PbCl_2 electrodes.⁴²

It is important for the ECs to exhibit high C_ϕ over a large voltage region. However, the voltage window available for the EC device is dictated by the operating pH and the thermodynamic stability of the pertinent species in the solution. Thus, in aqueous solutions, Ni and Co oxides are not suitable in acidic solutions and RuO_2 is unstable in alkaline media at high anode potentials. Pt-H is stable in acid and alkaline solutions and MnO_2 exhibits high charge storage capability only in unbuffered solutions, as the pH swings allow enhanced proton diffusion in and out of the MnO_2 lattice. The $\text{C-H}_2\text{SO}_4$ system undergoes corrosion beyond 0.8 V but up to 1 V; the corrosion rate is minimal so that a practical device can be built. To realize a large voltage window, a wide variety of solvents have

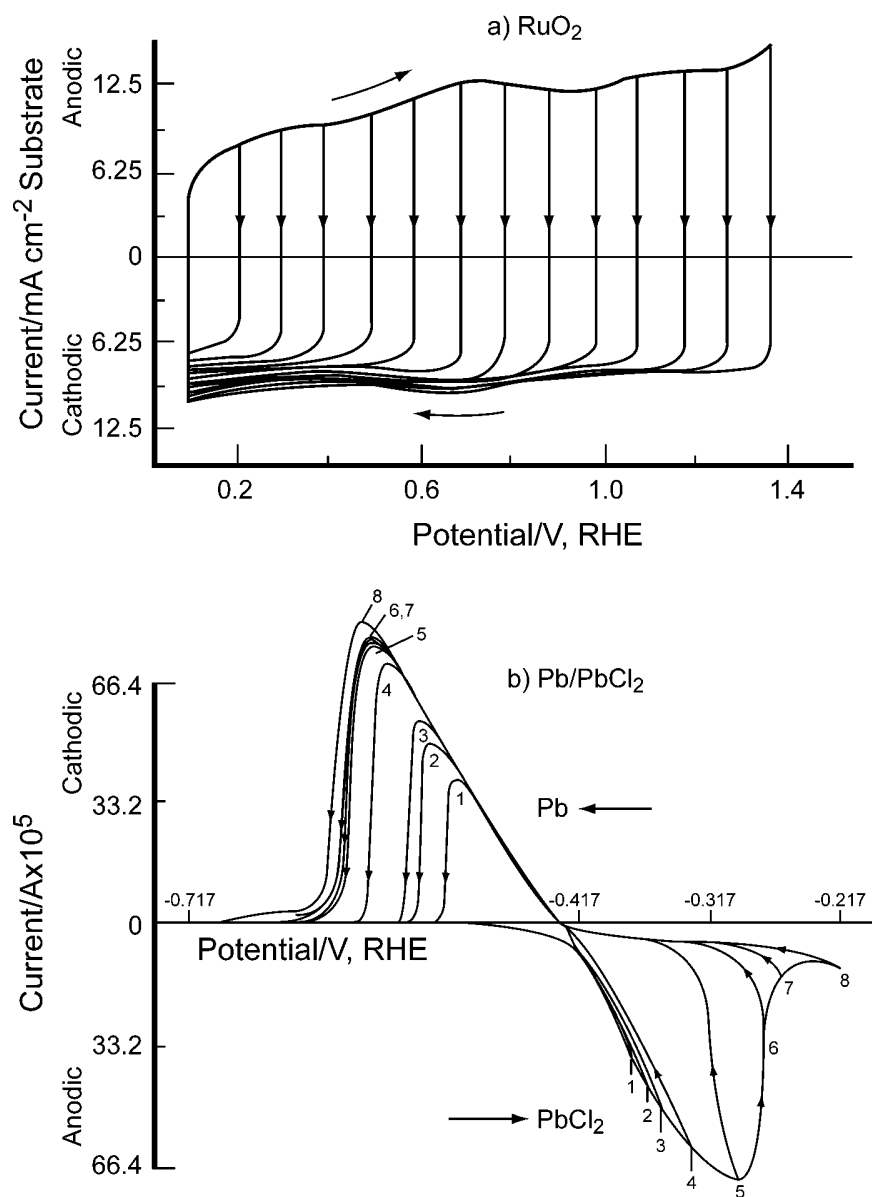


Figure 3.35. Cyclic voltammograms illustrating the reversible behavior of a ruthenium oxide electrode and the irreversible behavior of a lead/lead dichloride electrode. Reproduced by permission of the author.⁵⁰

TABLE 3.22.
Some Manufacturers of Electrochemical Capacitors

Aqueous medium	Non-aqueous medium
Symmetric design	
ECOND	Montena
ELITE	Maxwell
NEC	NESS
(PRI)	EPCOS
	Panasonic
	Okamura
Asymmetric design	
ESMA	Telecordia
Mega-C	

been examined. These include solid electrolyte such as RbAg_4I_5 , proton conducting ionomer membranes, solvents such as acetonitrile, propylene carbonate with alkali metal, or tetraalkyl ammonium cations with CF_3SO_3^- , $\text{N}(\text{CF}_3\text{SO}_2)^{-2}$, BF_4^- , PF_6^- , AsF_6^- and ClO_4^- anionic groups, and quaternary phosphonium salts in organic solvents. Based on lithium battery work, gel electrolytes (polyacrylonitrile or polyethylene oxide with an electrolyte salt cast into a film) were also studied. Of these, solid polymer electrolytes appear promising in terms of assembly and manufacturing ECs.

3.7.6.3. Applications and Economics. Electrochemical capacitors find applications in three major areas: consumer electronics, the automotive industry, and the industrial sector.⁴⁷ Consumer electronics can employ low-voltage ECs for digital wireless devices, memory back-up (e.g., clocks, VCRs), rechargeable tools, and appliances. Automotive applications include combined starter-generators, hybrid power systems, electric power steering, electric fork lifting, and use mid-voltage

TABLE 3.23.
Commercially Available Electrochemical Capacitors

Supplier	Voltage (V)	Capacity (F)	Resistance ($\text{m}\Omega$)	Time constant (s)	Wh/kg
Skelton Technology	3	47	5.2	0.24	10
Maxwell	3	2700	0.5	1.35	4.8
Ness	3	2650	0.25	0.65	5.1
Panasonic	3	1200	1	1.2	4.2
Montena	3	1800	1	1.8	5.6

TABLE 3.24.
Cost Comparison of Electrochemical Capacitors*

	\$/F
Large ECs(>20 kJ)	0.3 – 2
Small ECs	1 – 20
Al electrolytic capacitors	100 – 300
ECs-military	300 – 700
Tantalum capacitors	8000 – 13000

* commercial 5–10 V capacitors

ECs. High voltage ECs are for industrial uses such as magnetic actuators, battery load-leveling, and power-line conditioning. There are several companies throughout the world that are involved in the development and manufacture of ECs having a wide range of voltage and capacitance characteristics. Table 3.22 provides a list of some of these manufacturers,⁴⁸ and Table 3.23 lists some prototype and commercially available carbon-based ECs.⁴⁹ Table 3.24 provides a comparison of the costs of the ECs.^{47–49} The present costs of aqueous ECs are about \$ 100/kJ or \$ 359/kWh, and it is the goal of the EC manufacturers to cut the costs down to less than \$ 10/kWh.

3.7.6.4. Benefits to or from fuel-cell technology. The high power-density of ECs has made them attractive for use in hybrid configurations with batteries and fuel cells in electric vehicles and other load-leveling applications.⁵⁰ The EC, when coupled with a fuel cell or battery, provides the required power density for up-hill or accelerated driving while regenerative braking provides recharging. Two-types of hybrid systems are available:

- RuO₂-based EC/electrolytic capacitor, and
- Carbon-based EC/PbO₂/PbSO₄ or NiOOH/Ni(OH)₂. These are called asymmetric capacitors.

Figure 3.22 illustrates the Ragone plot, comparing the energy density and power density of fuel cells and batteries. Electrochemical capacitors are not viewed as replacements for either fuel cells or batteries but as complementary energy storage and delivery systems.

3.8. ELECTROCHEMICAL SENSORS

3.8.1. Background and Rationale

Chemical and electrochemical sensors were invented more than 50 to 60 years ago. These sensors may be defined as small portable devices that are used for measurement of concentrations of species, over a wide range (10^{-6} μ M to a few molar); these species are, in general, in the presence of many others. There are a large number of applications of sensors in university, government, and industrial research laboratories. A few examples are in analytical chemistry, environmental monitoring and remediation, the automotive industry, clinical diagnostics, and biomedical research. This Section is devoted only to electrochemical sensors; more details of sensor technology can be found in the references in Suggested Reading.

3.8.2. Principles of Technology

There are principally, four types of electrochemical sensors:

- ion-selective electrodes,
- sensors for measurements of gas analysis in liquids,
- electroanalytical sensors for measurements of concentrations of metallic ions in electrolytes, and
- sensors using enzyme electrodes, used in biochemistry and clinical studies.

The first ion selective electrode was for the measurement of the pH of an electrolyte. It utilizes a H^+ selective glass electrode, in the form of a membrane. This was followed by development of other glass electrodes, selective to ions such as Li^+ , Na^+ , K^+ , Cs^+ , Ag^+ , Tl^+ , NH_4^+ and also anions such as the halides. These electrodes are based on equilibrium potential, obeying the Nernst equation:

$$E = E_r + \frac{RT}{nF} \ln a \quad (3.79)$$

where E_r is the standard reversible potential and a is the activity of the ionic species. Since there is a logarithmic relationship between E and a , the sensitivity is not as high as with amperometric sensors.

Some of the electrochemical sensors, used for analysis of trace gases in electrolyte use fuel cell principles. To quote some examples, these are used for analysis of gases such as H_2 , O_2 , CO , H_2S , and Cl_2 . These sensors are used for measurements of limiting currents at electrodes for the oxidation or reduction of the above mentioned gases. This method is quite sensitive because the concentration of the gas, dissolved in the electrolyte is linearly related to the limiting current density.

A similar kind of electrochemical device is the voltammetric sensor. It is used widely for measurements of concentration of ionic species (metallic and negative

ions) in electrolytes. This device measures the current at set potentials. Here again, the concentration of the ions is linearly related to the current. An advantage of this method is that it can be used for detection of several ionic species in the electrolyte. This is done by varying the set potentials to different values that correspond to the regions of potentials where oxidation or reduction of the ionic species can occur. One difficulty of the method is that electrodes can be poisoned by impurities in the electrolyte. But there are means of cleaning up of the electrolyte to get rid of mainly organic impurities or to reactivate the surface of the electrode.

The fourth type of electrochemical sensors, enzyme-modified electrodes, has been making the most advances in the recent years. These are extensively used in biomedical applications, both *in vitro* and *in vivo*. One of the simplest ones will be briefly described. This type is used for measurement of glucose concentration in electrolytes, including blood. In one design, glucose oxidase is covalently bonded to a Ru^{2+} pentamine complex to electrochemically link the internal flavin group with the external redox mediators. A biocompatible gel (an epoxy resin) is used to bind the proteins and other electroactive materials. Other enzymes are also introduced to prevent interference from organic species such as ascorbate and urate.

Rapid advances have been made in chemical/electrochemical sensor technology using micro-fabrication and miniaturization methods. These include photolithographic techniques to design a surface with thin film deposition and oxide growth and silicon doping for fabrication of microelectronic circuits. Since the sensing element and signal conditioning electronics are on a single structure, the signal to noise ratio can be enhanced. Sensors have also been designed and developed for multi-elemental/ionic species analysis.

3.8.3. Applications and Economics

Several of these have been mentioned in the first Section. In respect to economics, sensors are small/ultra small devices. The manufacturing scale is very high.

3.8.4. Benefits to or from Fuel-Cell Technology

One of the most relevant benefits to fuel cells is the solid state sensor used for measurements of oxygen concentration in the exhaust gases from an automobile. It uses a solid oxide electrolyte, practically the same as in a SOFC, and it operates at a temperature of about 800 °C. The thin film technology, being developed for SOFCs, would be beneficial for further improvements in these sensors. Another similarity between the two technologies is in respect to measurements of dissolved gas as H_2 , O_2 , CO , and H_2S in electrolytes. Advances made in the composition and structure of fuel cell electrodes could benefit the development of new sensor electrodes.

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PROBLEMS

1. Calculate the thermodecomposition and thermoneutral voltage of diaphragm, mercury, and membrane cells at various temperatures. Discuss whether or not these cells can be operated at the thermoneutral voltage, and if so, why so and if not, why not?
2. Describe the anode, cathode and the overall reactions involved in electrolytic production of aluminum by the Hall-Hèrault process?
3. Calculate the operating and capital costs for producing 1000M tons of copper per year. What is the % of electricity and material costs used for producing one ton of copper?
4. What are the various anodic and cathodic reactions that can supplant the hydrogen evolution and oxygen evolution reactions to achieve energy savings in electro-organic processes?
5. Calculate the maximum capacitance that can be realized with pseudocapacitance based capacitors?